

**Melt Processability and Post-Processing Treatment
of High Temperature Semi-Crystalline Thermoplastics
for Extrusion Deposition Additive Manufacturing**

A Dissertation Presented for the

Doctor of Philosophy

Degree

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Dedicated to my loving parents, Kishore and Kathyayani, for their support and
motivation all through my life.

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ABSTRACT

Composites of high performance semi-crystalline thermoplastics are emerging as viable candidates for autoclave tooling applications, which typically demand good mechanical and thermal performance, as well as chemical resistance. With the growing demand for tooling, there is a need for versatile customizable tools that can be inexpensively manufactured with low lead times. Extrusion Deposition Additive Manufacturing (EDAM) technique can be extremely beneficial for the manufacture of low-cost composite tools with high degrees of customizability and short lead times. However, EDAM processes for such high temperature polymers can pose several challenges for extrusion and deposition due to their inherent properties as well as their thermal and oxidative responses. In addition, to use these printed parts in an application, the desired mechanical property requirements have to be realized. The use of semi-crystalline polymers in AM not only adds to the already existing complexity of mechanical anisotropy of the printed parts, but also makes the final part properties dependent on the crystallization in the deposited beads. For out of the oven EDAM processes, crystallization after extrusion and deposition takes place non-isothermally, further complicating crystallization mechanisms. This work encompasses strategies to address challenges encountered both, during deposition, as well as post-deposition, of commercial grades of carbon fiber reinforced poly (ether ketone ketone) (PEKK) and polyphenylene sulfide (PPS). The first section of this work involves determining the melt processability by evaluating the thermal and rheological characteristics of these materials under different processing conditions that can be encountered during EDAM processing. Establishing the link between rheological

properties and printing can guide the development of such new materials as well as printer design. The second section focuses on post-processing isothermal annealing as a strategy to enhance crystallinity, thereby improving the mechanical properties of printed carbon fiber reinforced PPS parts. In addition, a detailed analysis of the possibility of crosslinking in PPS, its effect on crystallinity and the mechanism dominating the changes in mechanical properties has also been discussed. Overall, this work provides a broad framework for developing high performance semi-crystalline thermoplastics for high temperature tooling applications employing 3D printed tools.

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1. Introduction

1.1. Motivation

The development of polymer matrix composites has been on-going for several decades owing to the wide range of properties and multifunctionality these materials offer, thereby leading to a myriad of applications in areas such as energy, aerospace, automotive, oil and gas, construction, biomedical, electronics, etc.¹⁻⁸. Polymer composites manufacturing processes such as injection molding, compression molding, layup process, resin transfer molding, casting, etc. typically require a rigid mold that defines the final shape of the component fabricated and such molds, dies and tools used in manufacturing are referred to as tooling⁹⁻¹⁰. Currently used tooling materials include metals and alloys such as aluminum, steel, invar, ceramics, or composite tooling made using epoxy based matrices¹⁰⁻¹¹. Metal and alloy based tools have the disadvantage of high manufacturing cost and lead time (since most of the tools are manufactured overseas) as well as coefficient of thermal expansion (CTE) mismatch between the tool and the composite part, leading to part distortion^{9, 11}. Ceramic tooling have the drawback of large thermal mass, thereby requiring high heat input to achieve the desired processing temperature, as well as the tendency to crack during cure¹⁰⁻¹¹. Epoxy based composite tooling, although help overcome the CTE mismatch issue, often do not meet the high temperature requirements for processing high temperature polymer matrix composites¹¹ and also make tooling expensive since in low volume productions, they are typically handmade, which adds to the manufacturing cost¹². Also, thermoset based tooling makes them non-recyclable and limit their shelf life. Therefore, the goal is to be able to manufacture tools using a process that is

faster, cheaper, with low energy requirement, and allows for on-site repair and modification of tools and by using materials which meet the desired mechanical and thermal performance for tooling (the application focus of this work being autoclave tooling). With this overall objective, this work explores the use of additive manufacturing (AM), or 3D printing process for processing high temperature semi-crystalline thermoplastic composites.

1.2. Extrusion Deposition Additive Manufacturing

Additive manufacturing (AM), most commonly referred to as 3D printing, is the process of building components by adding material layer by layer, with each layer being a thin cross-section of the part, derived from a 3D model data¹³. AM opens up several technological opportunities such as design customization with increased design complexity, flexibility in manufacturing, one step production of functionally integrated designs and reduction in materials waste. In addition, AM also offers economic advantages such as the reduction in assembly work, potential for simpler supply chains and shorter lead times, and localized production¹³⁻¹⁵. Additive manufacturing uses a wide variety of materials such as metals, polymers, ceramics, and composites. The use of polymers in additive manufacturing has been of significant interest due to its ease of processing and superior engineering performance. Moreover, it provides unique engineering and economic advantages such as high strength to weight ratio, versatility in applications, the ability to engineer tailored properties and relatively lower cost and energy requirements when compared to other materials.

Among the various polymer additive manufacturing processes, material extrusion deposition additive manufacturing (EDAM) process, often referred to in literature as fused deposition modeling (FDMTM) or fused filament fabrication (FFF), is the most widely used technique for printing a variety of thermoplastics and composites¹⁶⁻²². A majority of the initial commercially available 3D printing platforms have been small-scale printers (Figure 1.1) utilizing polymer filament-based feedstock which is resistively melted and deposited on a heated print bed. Typically these printers offer small build volumes of 0.03 to 0.3 m³ with deposition rates in the range of 15 to 85 cm³/h, making them less suited for printing large parts, which can better utilize the economic advantages of such AM technologies²³. Scaling up of extrusion AM process has been possible with the development of large format print platforms such as the Big Area Additive Manufacturing (BAAM) system (Figure 1.2). The BAAM system has a build volume of 30 m³, temperature capability of up to 510 °C, with the ability to deposit a variety of thermoplastics and composites feedstock at rates as high as 50 kg/hr, thereby making the process bigger, faster and cheaper when compared to several other existing material extrusion systems²³⁻²⁶. In addition, this system uses pelletized feedstock, similar to the ones used in traditional polymer processing such as injection molding. This makes a wide variety of commercially available common thermoplastics and composites readily available for BAAM and also reduces the cost of feed materials by almost 20 times in comparison to the filament feedstock²³. Such flexibility also enables building functionally graded components, leading to further possibility of optimizing cost and performance for 3D printed components²⁶.

The BAAM system operates using a single screw extruder mounted on a gantry as shown in Figure 1.3. Dried pellets are fed into the extruder where they are heated and melted as they move along the screw and finally extruded through the circular orifice at the exit. The material is deposited on a heated print bed in an environment that is not temperature controlled. Large-scale printed components find applications in areas such as automotive, aerospace, tooling and energy sectors. In order to realize the potential of these production scale systems and expand the functional applications of printed components, there is a need to develop new materials that are compatible with such large-scale systems and print components that meet the desired end use properties. Some of the materials that have been used for printing on the BAAM system include fiber reinforced composites of acrylonitrile butadiene styrene (ABS)^{23, 25}, polylactic acid (PLA), as well as high performance amorphous thermoplastics such as poly(phenylsulfone) (PPSU)^{24, 27}, poly(ether imide) (PEI)^{25, 28}. Since this system operates outside of an oven, the use of fiber reinforced composites have been found to be advantageous to reduce distortion and warping in the printed parts by lowering of linear coefficient of thermal expansion by about an order of magnitude^{16, 23, 29}.

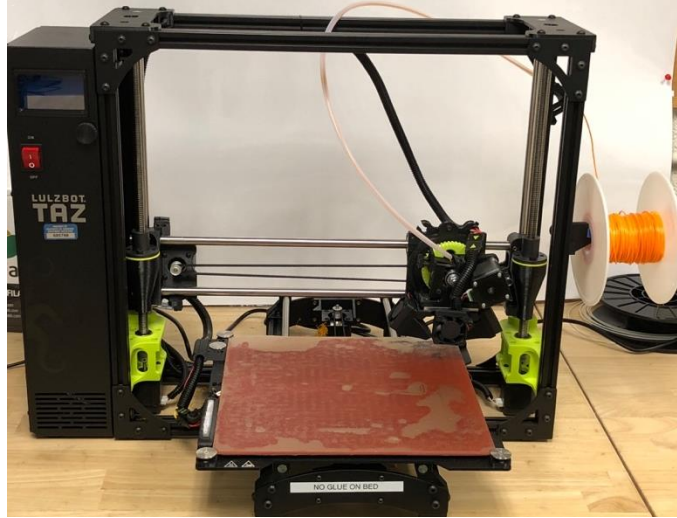


Figure 1.1 Filament based extrusion AM platform.



Figure 1.2 Big Area Additive Manufacturing (BAAM) system. Photo courtesy of Oak Ridge National Laboratory, US Dept. of Energy.



Figure 1.3 BAAM extruder set-up. Photo courtesy of Oak Ridge National Laboratory, US Dept. of Energy.

1.3. High Temperature Semi-Crystalline Thermoplastics

High temperature or high-performance thermoplastics are polymers that are used in advanced applications that demand such as thermal stability, high continuous use temperature, chemical, wear and flame resistance, and superior mechanical properties³⁰⁻³². These thermoplastics are based on aromatic polymers, thereby increasing the rigidity of the backbone chains (when compared to aliphatic thermoplastics) and offer superior mechanical, chemical and thermal performance. Some of the commonly used high performance 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)^{30-31, 33}. The presence of crystallinity in semi-crystalline polymers offer advantages over amorphous thermoplastics with respect to higher range of continuous use temperature, the ability to use the material at temperatures even above the glass transition temperature (T_g) for short spans without much loss in modulus, better resistance to creep deformation, excellent chemical and wear resistance^{30, 34-36}. The dependence of some of these properties on crystallinity offers an interesting pathway to tailor the final properties of a manufactured part by controlling crystallization parameters.

This work focuses on two high temperature semi-crystalline matrices, poly (ether ketone ketone) (PEKK) and polyphenylene sulfide (PPS), and their carbon fiber reinforced grades as candidates for extrusion additive manufacturing.

1.3.1. Poly (ether ketone ketone) (PEKK)

Poly (ether ketone ketone) (PEKK) is a semi-crystalline high-performance thermoplastic belonging to the family of poly (aryl ether ketones) (PAEKs). These materials find applications in aerospace and automotive components, medical applications, electronics, and oil and gas exploration^{30-31, 35, 37-38}. They have superior mechanical performance, chemical resistance and service temperatures, determined by the regularity and rigidity of their backbone chain formed by aryl, keto and ether linkages^{35, 39}. The ratio and sequence of keto to ether linkages determines the thermophysical properties of such polymers. An increase in keto linkages increases the rigidity of the monomer, thereby leading to a higher glass transition temperature (T_g)⁴⁰⁻⁴¹. In addition, increasing keto linkages also increases the interaction and packing of the aryl groups, thereby increasing the crystal binding energy and melting temperature (T_m)^{38, 40}. Among the various materials in the PAEKs family, PEKK has relatively high level (~ 67%) of keto linkages (Figure 1.4a) and exhibits a high melting temperature of ~ 400 °C, which is close to the degradation temperature of PAEKs polymers, making it difficult to process these materials^{38, 40}. However, the melting temperature can be significantly lowered by synthesizing PEKK as a copolymer with meta-linkages in the backbone chain. Figure 1.4b represents the structure of PEKK copolymer with terephthaloyl (T) (para-linkage) and isophthaloyl (I) moieties (meta-linkage). The introduction of isophthaloyl moiety lowers the melting temperature, thereby the processing temperature of PEKK⁴². By varying the T/I ratio, thermophysical properties and crystallization behavior of the polymer can be modified.

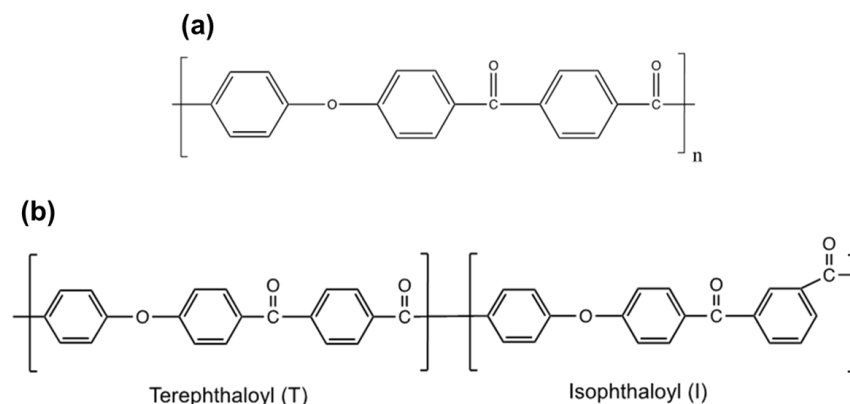


Figure 1.4 Structure of PEKK (a) Homopolymer and (b) Copolymer.

Lowering the proportion of terephthaloyl groups lowers the rate of crystallization as well as the melting point and desired PEKK grades can be chosen depending up on the application³⁸.

1.3.2. Polyphenylene Sulfide (PPS)

Polyphenylene sulfide (PPS) is another semi-crystalline aromatic high temperature thermoplastic in the family of polyarylene sulfides with structure as shown in Figure 1.5³⁰. PPS offers excellent chemical resistance, flame resistance, stable dielectric and insulating properties, and good mechanical properties at elevated temperatures and finds applications in automotive, aerospace sectors⁴³⁻⁴⁵. PPS can be of three types; linear, branched, or slightly crosslinked, depending up on the polymerization process and thermal treatment that it is subjected to³⁴, thereby leading to properties dependent on prior processing conditions. Apart from offering the advantages of a semi-crystalline polymer, one of the other interesting properties of PPS is its ability to undergo structural changes in the form of chain

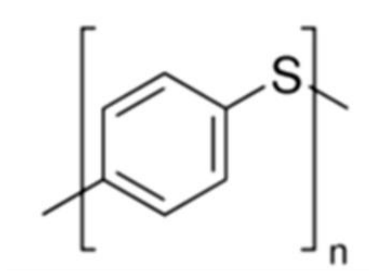


Figure 1.5 Structure of PPS.

extension, branching and crosslinking when heated in air at temperatures above the melting point (melt state) or slightly below the melting point ^{34, 43-49}. This property adds to the complexity of processing such materials as well as provides another mechanism to alter the properties of parts produced.

1.4. Existing Challenges and Research Objectives

EDAM process for thermoplastics can be divided into two parts, ‘deposition’, which involves melting and extrusion of the material, and ‘post-deposition’, which involves conditions and processes encountered after depositing the material on to the print bed.

Extrusion Deposition

EDAM of high temperature semi-crystalline thermoplastic composites requires a good understanding of the relationship between process, structure and properties during deposition as well as for post-deposition conditions. The chemical structure of these polymers, as indicated in the previous section, and the addition of fillers can alter the viscoelastic properties of the polymers, thereby influencing their melt processability. In addition, the deposition process parameters can also impart changes to the structure and

flow behavior of these high temperature polymers, thereby influencing the processability and the quality of beads (layers) extruded. This makes the understanding of effect of various processing parameters on rheological properties critical, prior to processing, especially to reduce the risk of downtime and material waste for large-scale print platforms. Also, determination of rheological properties can provide guidelines for better printer design, especially for processing new materials. It should be noted that for the chosen materials, there are very limited works reported on the rheological behavior of these materials, especially fiber reinforced systems over a wide range of shear rates ($0.001 - 5000 \text{ s}^{-1}$)^{40, 50-52}. Also, in the EDAM field, the development of these materials has been very recent and focused on filaments for fused filament fabrication (FFF) printers. 3DXTECH has developed PPS and PEKK filaments⁵³⁻⁵⁴ and Stratasys has developed PEKK filaments⁵⁵ (without fiber reinforcement).

Post-deposition

Mechanical properties of 3D printed components, in general, are not just dependent on the material properties but also on the processing conditions and print parameters used for deposition^{23, 56-57}. For the large-scale BAAM system wherein, there is no temperature-controlled chamber enclosing the print bed, mechanical properties of the parts are also dependent on part geometry (which determines the cooling rate) and thermal mass of the bead, as these parameters also determine the extent of bonding between layers. In several previously reported works on amorphous thermoplastic composites, mechanical anisotropy i.e., strength of the parts across successive layers in the build direction (z-direction) was observed to be significantly lower than the corresponding in-plane strength (x-y

directions)^{23, 25, 57}. Such thermal history dependent mechanical properties were observed even for amorphous materials, as the primary bonding mechanism between the printed layers is thermal fusion and polymer inter-diffusion, which depends up on the thermal energy of the thermal energy of the semi-molten polymer and area of contact between the layers^{22, 58}. Printing semi-crystalline materials on the BAAM system to obtain parts with desirable mechanical properties is even more challenging as the mechanical properties of these parts depend not only on thermal fusion and polymer inter-diffusion mechanism but also on the development of crystallinity in the deposited material. Since BAAM processing involves non-isothermal crystallization of the deposited bead, temperature variations within a bead (surface of the bead can cool off faster than the bulk of the bead) can further complicate crystallization kinetics and crystal morphology.

In an effort to enhance overall crystallinity in printed components for improved mechanical performance, this work investigates the process of post-processing heat treatment, i.e., isothermal annealing of the printed parts in an oven after the deposition and completion of part printing. Isothermal annealing is a technique that has been used in the molding industry traditionally for semi-crystalline polymers to increase the degree of crystallinity of the molds, thereby enhancing mechanical properties. However, the thermal history and processing conditions that the material experiences are different in molding when compared to non-isothermal crystallization conditions in EDAM. Studies reporting crystallinity developed in 3D printed parts are very recent and limited, primarily on PLA, PEEK deposited using small scale EDAM process⁵⁹⁻⁶⁰. Few recent studies report the effect of post-processing annealing of neat PPS parts printed on small scale EDAM platform⁶¹⁻⁶².

Geng, P. et.al., showed that annealing samples with initially low degree of crystallinity led to an increase in the degree of crystallinity, thereby favoring tensile strength and fracture toughness but lowering impact strength⁶². Studies by Fitzharris, E.R., et.al., on small scale EDAM of neat PPS parts indicated annealing to improve mechanical properties. Increasing annealing temperatures (room temperature, 140 °C and 180 °C) caused both tensile strength and modulus to increase due to an increase in crystallinity. However, this study does not discuss other mechanisms simultaneously in play during annealing (such as crosslinking)⁶¹.

Despite these studies reported in literature, there has not been any work reported on

- (i) The effect of annealing on the mechanical properties of 3D printed short-fiber reinforced composites, more specifically for parts with thermal history created by large-scale EDAM processing.
- (ii) Variation in mechanical properties due to annealing across a range of temperatures for printed PPS (neat or CF reinforced). Most of the reported studies are on room temperature mechanical properties.
- (iii) Effect of annealing on the development of crystallinity and crosslinking in PPS in different sections across a part (surface to bulk) for molded or printed components.

Specific Research Objectives

With the overarching objective of being able to print carbon fiber reinforced high temperature semi-crystalline thermoplastics on large-scale extrusion AM system and obtain components with good mechanical properties, this work focuses on two research questions for the challenges discussed:

- (i) Deposition: What all process parameters influence the extrusion of the chosen PEKK and PPS grades? Can rheological characterization be used to identify appropriate processing conditions for extrusion deposition of the chosen materials?

This work on melt processability will be discussed in Chapter 2.

- (ii) Post-deposition: Can post-processing isothermal heat treatment enhance mechanical properties of PPS parts? If so, what mechanism drives or dominates the improvement in mechanical properties?

This work on post-processing treatment will be discussed in Chapter 3.

2. Melt Processability of PEKK and PPS Composites

2.1. Introduction

Extrusion deposition additive manufacturing (EDAM) process is one of the most widely used AM technique for printing components with polymers and composite materials^{16-22, 63}. Some of the most commonly used thermoplastic materials for this technique include acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), nylons, polyamides, high performance thermoplastics such as polyphenylsulfone (PPSU)^{24, 27}, polyetherimides (PEI)^{28, 64}, polyamides, poly(ether ketone ketone) (PEEK) etc. Blends of these thermoplastics⁶⁵, thermoplastic matrix composites with metal powder fillers⁶⁶, inorganic additives^{19, 65}, and fibers¹⁶ have also been investigated as candidates for EDAM processing. In the case of high temperature semi-crystalline thermoplastics for EDAM, some of the reported efforts have been on investigating the properties of components printed using PPS⁶¹⁻⁶², PPS reinforced with carbon fibers (CF)⁶⁷, and PEEK⁶⁸, etc. Processing high temperature semi-crystalline polymers in EDAM pose some challenges due to factors such as:

- (i) High temperatures required in the printer (well above the melting point of the material).
- (ii) Short processing window as they can undergo thermal degradation.

Large-scale systems such as the BAAM, makes it possible to attain temperatures high enough for processing materials like PPS and PEKK. However, using such a production scale system that requires several pounds of the feed material to process, investigating materials not commonly used in EDAM increases the risk of material waste

and system downtime. An understanding of the material thermal and flow properties is essential prior to processing to determine suitable printing conditions as well as understand possible material failure or issues that may occur during processing.

Overall Objective: Melt processing of the chosen PEKK and PPS grades to be able to extrude them on EDAM platform.

Primary Research Questions

- (i) What is the effect of key processing parameters on the melt flow characteristics of the chosen materials?
- (ii) Can rheological characterization be useful to identify suitable processing conditions to extrude (flow through the nozzle) the chosen PEKK and PPS grades on EDAM platform?

Framework

For melting and extrusion of the chosen material, the key parameters that can be controlled prior to and during deposition include processing temperature, shear rate during extrusion (by controlling the flow rate and nozzle geometry), processing environment (in the extruder) and the intrinsic properties of the feed material such as the chemical structure and filler composition (Figure 2.1). A systematic approach to understand the effect of these parameters on thermal and flow properties of the feed material at different shear rates encountered in printing (as indicated in Figure 2.1), prior to deposition is essential. This provides a guideline for setting print conditions for new materials, enables a better understanding of instabilities that can occur during printing, and can also be used to predict the printability of new materials for a set of desired process parameters. This approach,

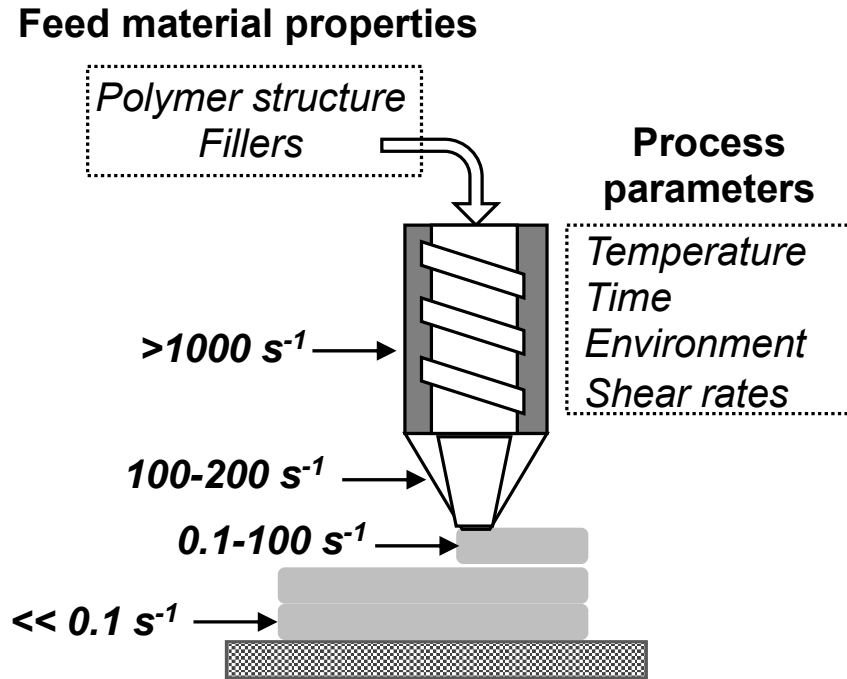


Figure 2.1 Schematic of BAAM process.

although can be applied to any material extrusion AM platform, is more beneficial for systems such as the BAAM as it helps reduce the risk of downtime as well as minimize material waste.

The first step in the approach discussed is the determination of suitable processing temperature window for deposition, which starts with the characterization of thermal properties of the feed material to determine the upper and lower processing temperature bounds. This has been performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine the degradation onset temperatures (DOT) and melting temperatures (T_m) respectively. Upon determining suitable temperature range, rheological characterization of feed materials has been performed under various conditions of temperature, shear rate and processing environment (under air or inert gas). These

controlled process parameters enable the understanding of viscoelastic behavior of these materials, which greatly influences the ability to extrude and deposit as well as meet the post-deposition properties requirements.

2.2. Experimental

2.2.1. Materials

Five different grades of Kepstan[®] PEKK pellets (Figure 2.2), obtained from Arkema Inc., were used in this work. The three unreinforced (neat) grades studied had T/I ratio of 60/40, 70/30 and 80/20 and the other two grades were short carbon fiber (CF) reinforced (CF 30 wt.% and CF 40 wt.%) in the 80/20 neat matrix. For PPS, three different grades of pellets (Figure 2.3) obtained from Techmer PM LLC, were used. One was unreinforced (neat) Fortran[®] neat PPS and the other two were short carbon fiber (CF) reinforced (CF 40 wt.% and CF 50 wt.%) in the same neat matrix.



Figure 2.2 Different grades of PEKK studied.

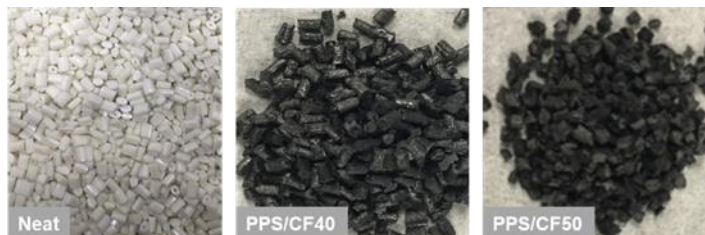


Figure 2.3 Different grades of PPS studied.

Prior to all tests, all PEKK pellets were dried at 120 °C for 6-8 hr, neat PPS pellets dried at 120 °C for 3 hr and filled PPS pellets dried at 130 °C for 4 hr.

2.2.2. Thermal Analysis

As the first step, to define the upper processing temperature limit, degradation onset temperature (DOT) was determined by performing thermogravimetric analysis (TGA) using TA Instruments Q500 system. Samples (about 5-7 mg each) were heated in air from 25 °C to 600 °C at 10 °C/min to determine the temperature at which there is greater than 1% weight loss. The lower limit of processing temperature was determined by performing differential scanning calorimetry (DSC) analysis on TA Instruments Q2000 system. Two heating cycles were performed at 10 °C/min from 25 °C to 375 °C or 400 °C for different PEKK grades and up to 350 °C for the PPS grades and the cooling cycle was at 5 °C/min. All DSC scans were done in nitrogen environment using a sample mass of about 5-7 mg in each case.

2.2.3. Rheological Analysis

Small Amplitude Oscillatory Shear (SAOS) Tests

To determine the effect of temperature, environment, time, shear and fillers on the dynamic rheological properties of the chosen materials, small amplitude oscillatory shear tests were performed on Discovery Hybrid Rheometer (DHR-2) from TA Instruments (Figure 2.4). The test fixture comprised of 25 mm disposable parallel plates on which pellets were directly melted between the plates using melt rings prior to each test. The gap between the plates was maintained between 1.6-2.3 mm for all the test samples. All tests

were performed at two candidate test temperatures selected based on thermal analysis. The first set of tests involved amplitude sweep tests wherein the polymer melts were subjected to oscillatory shear of varying amplitudes (0.001- 100%) at a constant frequency (ω) of 10 rad/s to monitor the change in dynamic moduli with oscillatory strain. This was done to determine the linear viscoelastic (LVE) regime, i.e. the oscillatory strain up to which there is no significant variation in storage modulus (G'). This indicates the region wherein the deformation is small enough such that the polymer structure remains unaltered. Upon selecting a suitable strain value in the LVE, isothermal time sweep tests were performed at a constant angular frequency (10 rad/s) for 10 min to determine the variation of dynamic moduli and complex viscosity (η^*) with time. These tests were used to determine the thermal stability of the material by characterizing the possibility of structural changes taking place with time. The test environment was air for all the amplitude and time sweep tests.

Based on the thermal stability of the different grades of PEKK and PPS in air, frequency sweep tests were performed in either air or nitrogen environment at all the chosen test temperatures to determine the variation in dynamic properties with frequency.

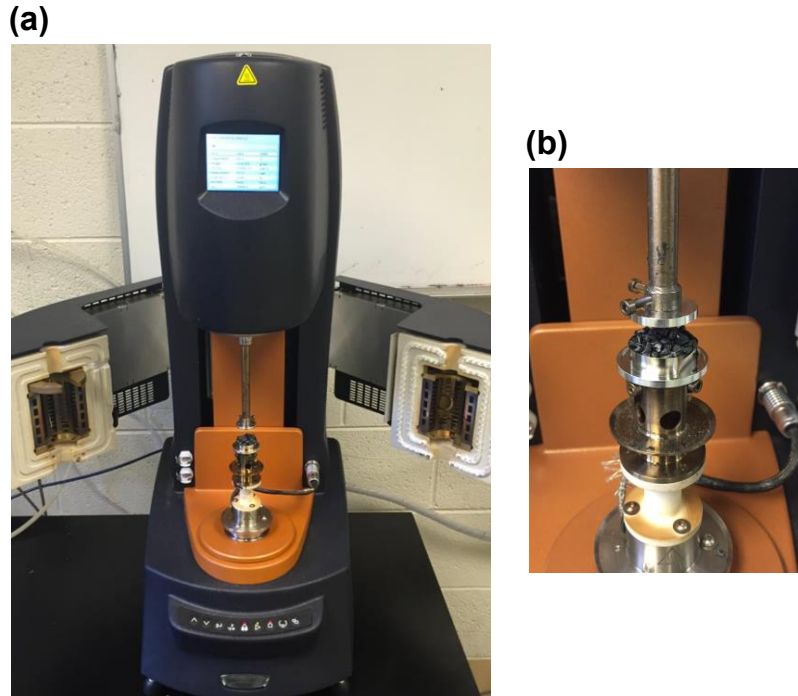


Figure 2.4 (a) Rotational rheometer and (b) Parallel plates fixture.

Steady Shear Tests

To understand the effect of high shear rates on melt viscosity, steady shear tests were performed on a Dynisco LCR 7001 capillary rheometer (Figure 2.5) for shear rates in the range of $5000\text{--}5\text{ s}^{-1}$ in air using a die with orifice diameter 0.75 mm, entrance angle 120° and L/D of 20. About 10 g of material was used for each test and the pellets were allowed to heat up in the barrel for ~ 10 min before the start of the test to ensure complete melting. Such steady shear tests are more representative of the extrusion process in AM since they not only cover the shear rate ranges used in such processes, but also factor in the effect of orientation of polymer chain and fillers in the flow direction.



Figure 2.5 Capillary rheometer.

2.2.4. Extrusion on EDAM Platform

To determine the extrusion capabilities of the chosen grades on EDAM platform using the processing conditions identified from thermal and rheological characterization, extrusion trials were performed on both small-scale FFF system as well as the large-scale BAAM system.

Trials on Fused Filament Fabrication (FFF) Platform

For extrusion on FFF system, filaments were first fabricated using a Filabot EX2 filament extruder, operating using a single screw extruder (Figure 2.6), from all the five grades of PEKK and three grades of PPS. Using temperatures identified from thermal and rheological analysis, and by varying screw speed and nozzle size, filaments were extruded

from the pre-dried pellets with a target diameter of 1.75mm. The extruded filaments were gently guided and rolled up under ambient conditions with minimum stretching. The fused filament fabrication printer system used for the extrusion trials were Makergear M2 and a Solidoodle 3, modified to work at temperatures as high as 400 °C using an E3D V6 all metal hot end. The nozzle diameter on the printers ranged from 0.6 mm to 1 mm, depending on the grade extruded.

Trials on the Big Area Additive Manufacturing (BAAM) System

Print trials on the BAAM system were conducted for the carbon fiber reinforced grades of PPS and PEKK. As mentioned in the previous section, printing large parts with carbon fibers helps lower warping and distortion^{16, 23}. PPS 40CF, PPS 50CF, and PEKK 80/20 40CF were printed using a nozzle of diameter 7.62 mm at temperatures in the range identified for rheological characterization⁶⁹⁻⁷⁰.



Figure 2.6 Filament extrusion.

2.3. Results and Discussion

2.3.1. Thermal Analysis

Figure 2.7 (a) and (b) represent TGA thermograms for the five PEKK grades. The data indicates all five grades of PEKK to be stable up to 500 °C without significant weight loss (less than 1%). For the PPS grades (Figure 2.8), all three grades exhibit stability at least up to 400 °C.

Figure 2.9 represents DSC thermograms indicating the second heating cycle for the five PEKK grades and Figure 2.10 represents the thermogram for the three PPS grades. The obtained inflection points of the glass transition temperature (T_g) and peak melting temperatures (T_m) have been reported in Table 2.1. Note that for the filled PPS grades, T_g was not detectable from the DSC thermograms for the heating rates used. Based on the TGA and DSC analysis, multiple processing temperatures (T_p) for further tests were identified at least 15 °C above T_m and well below the DOT (as shown in Table 2.1). For PEKK, the maximum temperature was limited to 390 °C. Although there are no volatiles given out up to 500 °C, PAEKs such as PEKK can undergo structural modifications in the form of branching and crosslinking above 400 °C, as reported in literature⁴⁰, as well as from some studies done on rheological behavior of these materials above 400 °C⁷¹.

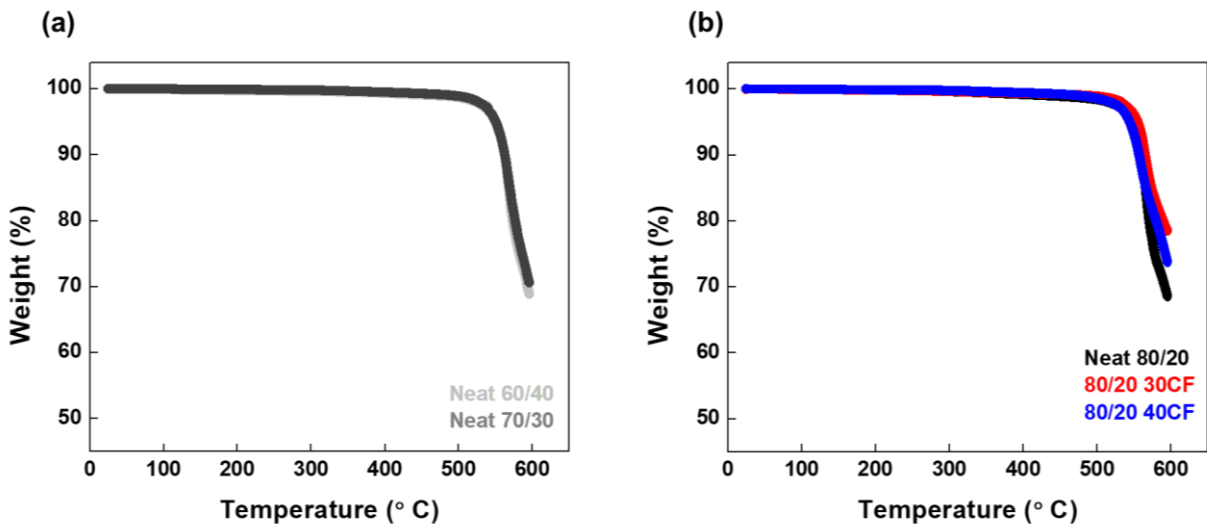


Figure 2.7 TGA of PEKK grades.

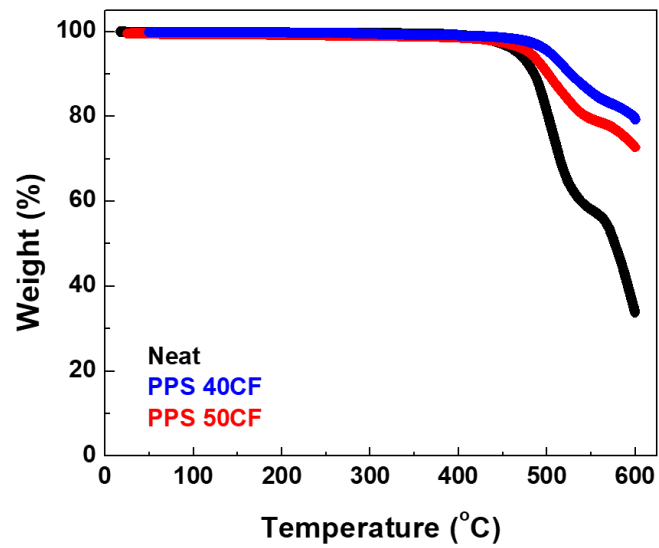


Figure 2.8 TGA of PPS grades.

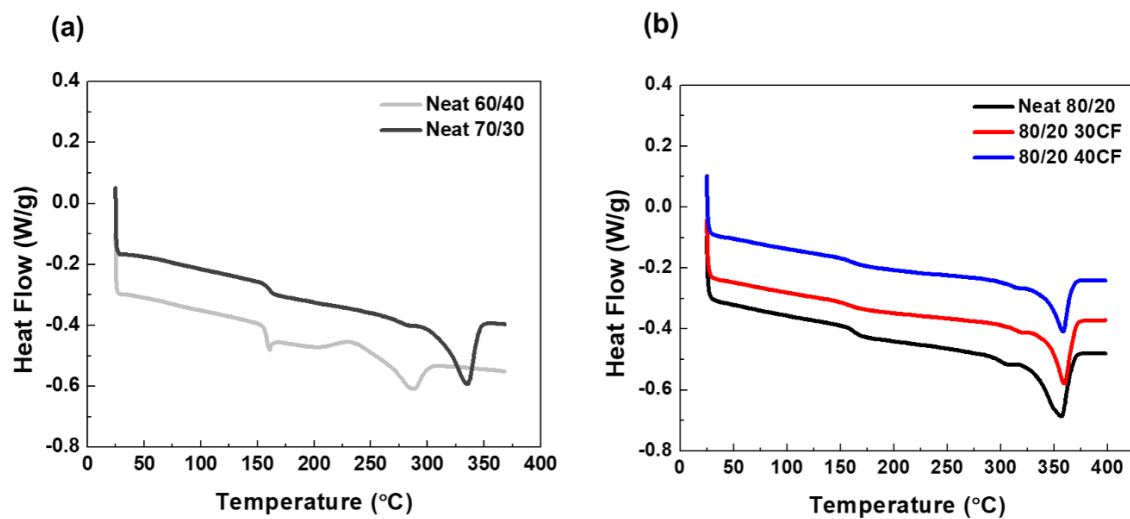


Figure 2.9 DSC analysis of PEKK grades.

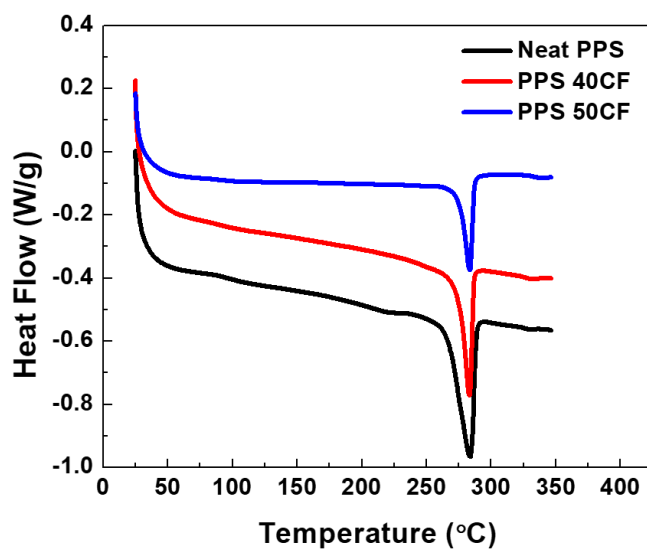


Figure 2.10 DSC analysis of PPS grades.

Table 2.1 Thermal analysis of the chosen materials.

Materials		DOT (°C)	T_g (°C)	T_m (°C)	T_p (°C)
PEKK	Neat 60/40	> 500	158	288	335, 350
	Neat 70/30		161	335	350, 375
	Neat 80/20		158	361	375, 390
	80/20 30CF		159	360	375, 390
	80/20 40CF		158	358	375, 390
PPS	Neat PPS	> 400	97	283	300, 315, 330, 345
	PPS 40CF		-	283	300, 315, 330, 345
	PPS 50CF		-	283	300, 315, 330, 345

2.3.2. Rheological Analysis

Small Amplitude Oscillatory Shear (SAOS) Tests for PEKK

Thermal Stability Tests

Figure 2.11 (a-c) represents the variation in storage modulus (G') and loss modulus (G'') with time for the three neat grades (60/40, 70/30 and 80/20) respectively. Time sweep tests were performed in air at the two chosen candidate temperatures for each grade using a strain value of 1% (within the LVE of the three neat grades). Table 2.2 shows the variation in complex viscosity (η^*) with time. Analysis of Figure 2.11 shows that all three neat grades of PEKK exhibit higher G'' than G' across all test temperatures, indicating that the material in melt state is more viscous than elastic at the chosen processing temperatures. An increase in temperature lowers both moduli and viscosity; however, with time, both moduli and η^* show some increase, which has been observed to be greater for 70/30 and 80/20 grades than 60/40. This increase can be attributed to structural changes taking place due to possible crosslinking in the material with time (increase in elastic behavior), which further increases with increasing temperatures. Such crosslinking reactions in air have been observed and reported for other PAEKs such as PEEK at elevated temperatures⁷². Changes in viscosity behavior due to thermal effects on polymer structure has been commonly reported for other high-performance materials as well as polymers such as low-density polyethylene (LDPE) in oxidizing environment^{39-40, 73}. However in this work, any increase in viscosity in the range of 20% or lower in isothermal time sweep tests has been considered to be of lesser significance and in the acceptable range for AM processing since the residence time on AM systems is much lower (~ 60 s) and the material also experiences

higher shear rates ($\sim 100\text{-}200\text{ s}^{-1}$ at the nozzle), which can possibly delay any crosslinking process. Hence, the three neat grades studied exhibit low viscosity build up and good thermal stability that make them suitable for AM processing for short residence time in air.

Figure 2.12 (a-c) represents the variation of dynamic moduli and complex viscosity with time for the three 80/20 grades (unreinforced and two carbon fiber reinforced grades) at the two candidate test temperatures of 375 °C and 390 °C. The LVE strain amplitude used was 1% for neat and 0.04-0.06% for the two filled grades. The moduli data shows an increase in both G' and G'' with increasing filler content at both temperatures. However, unlike the behavior observed for the neat grade, for the filled grades, G'' does not remain above G' for the full 10 min, indicating that the material starts to become more elastic with time in air. For the 40 wt.% CF reinforced (80/20 40CF) grade, it can be seen that the cross over point (where $G'' = G'$) occurs at $\sim 300\text{ s}$ at 375 °C and at $\sim 100\text{ s}$ at 390 °C. The increase in G' over time can be attributed to possible structural changes occurring in the material in the form of crosslinking, which could be accelerated by the presence of sizing (functional groups applied as coatings to carbon fibers to enhance filler-matrix interactions). The effect is also observed as an increase in complex viscosity of 47% and 64% respectively at 375 °C and 390 °C after 10 minutes for 30 wt.% CF grade and of 67% and 102% for 40 wt.% CF grades under similar conditions. This indicates that increasing the filler content and increasing the operating temperature reduces the thermal stability of the material over time. Also, higher fiber loading can also lead to a higher viscosity at elevated temperatures (as observed for 80/20 40CF).

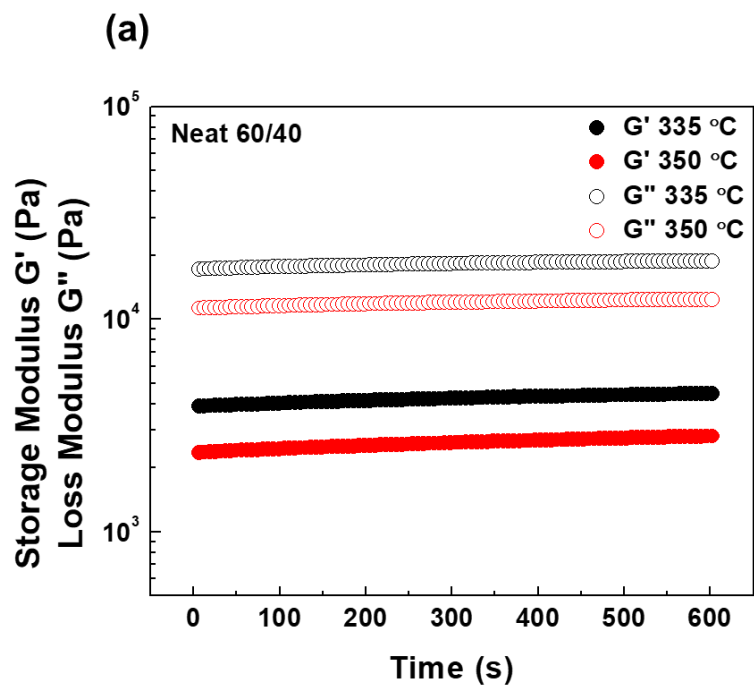
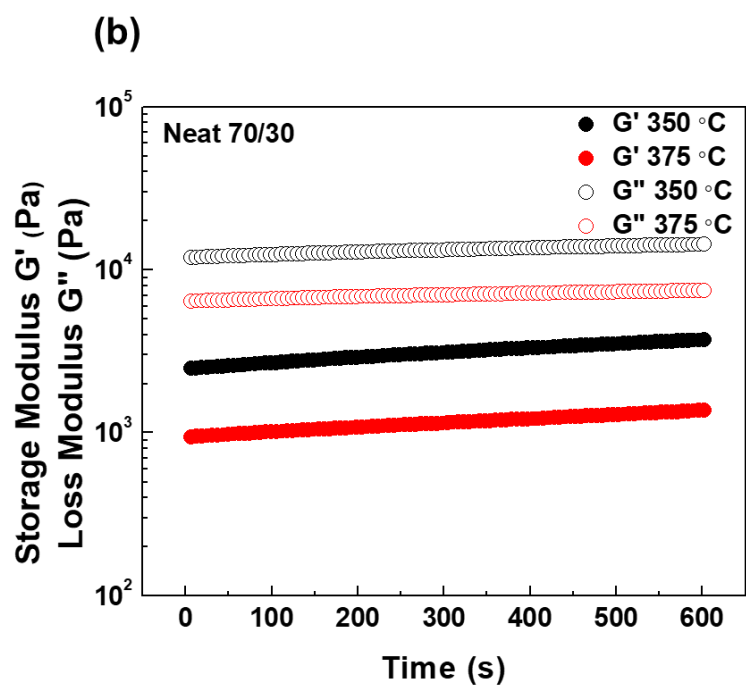


Figure 2.11 Time sweep tests at candidate processing temperatures in air for neat PEKK grades (a) 60/40, (b) 70/30 and (c) 80/20.

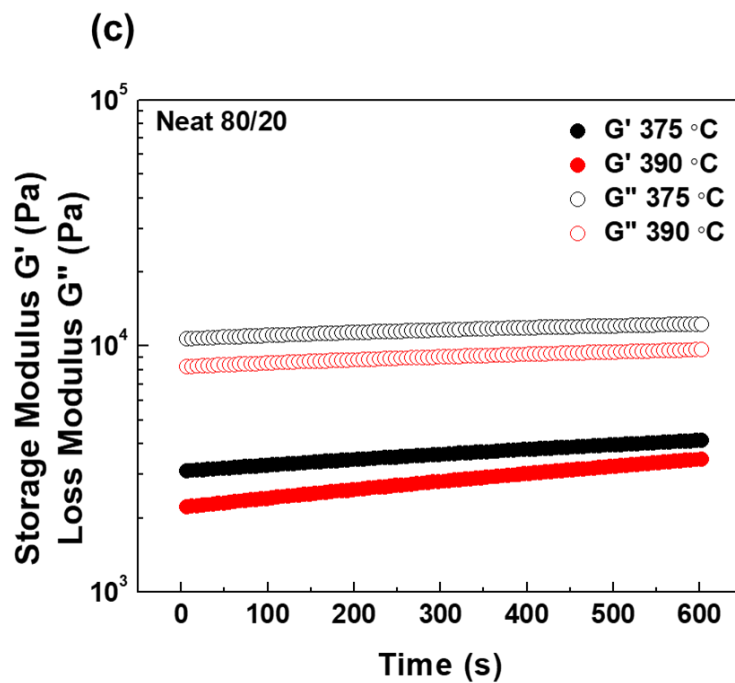


Figure 2.11 (continued).

Table 2.2 Variation of complex viscosity with time for neat PEKK grades.

Neat Grade	Test Temperature (°C)	η^* at t=6 s (Pa.s)	η^* at t=600 s (Pa.s)	% Increase
60/40	335	1761	1926	9.3
	350	1149	1271	10.6
70/30	350	1215	1478	21.6
	375	647	757	17
80/20	375	1111	1294	16.5
	390	851	1025	20.4

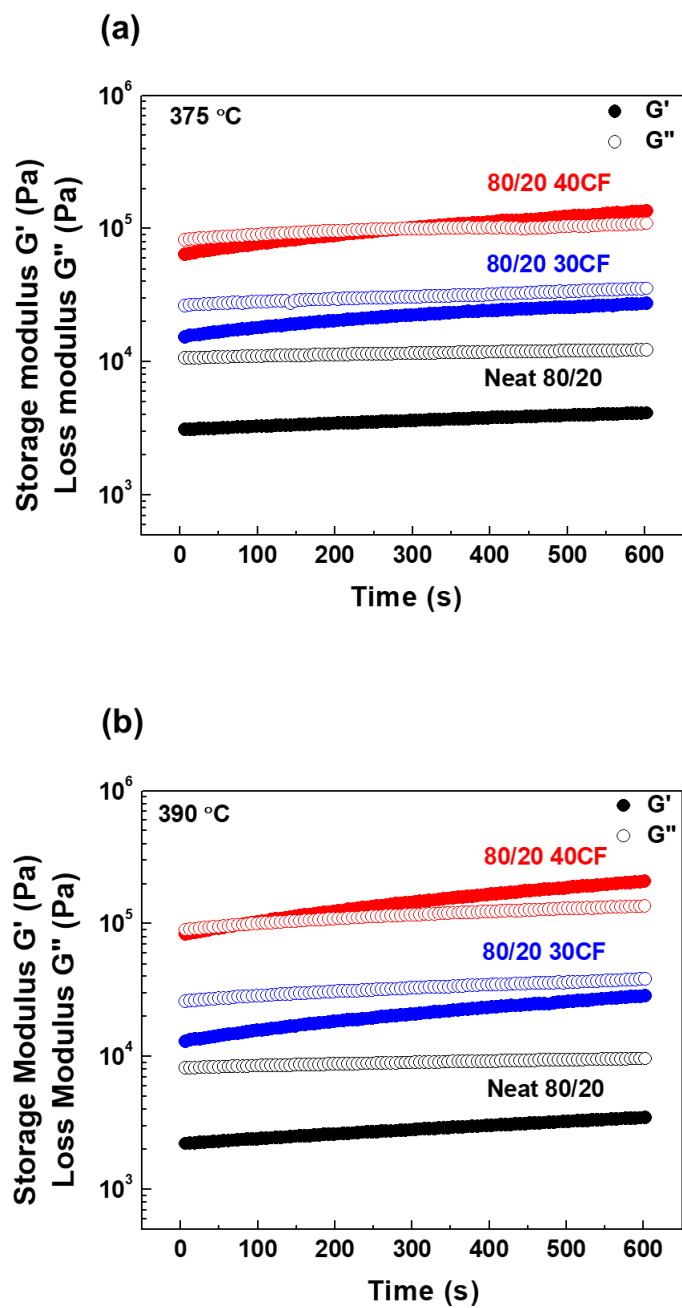


Figure 2.12 Time sweep tests in air for PEKK 80/20 grades; (a) Dynamic moduli at 375 °C, (b) Dynamic moduli at 390 °C and (c) Complex viscosity at 375 °C and 390 °C.

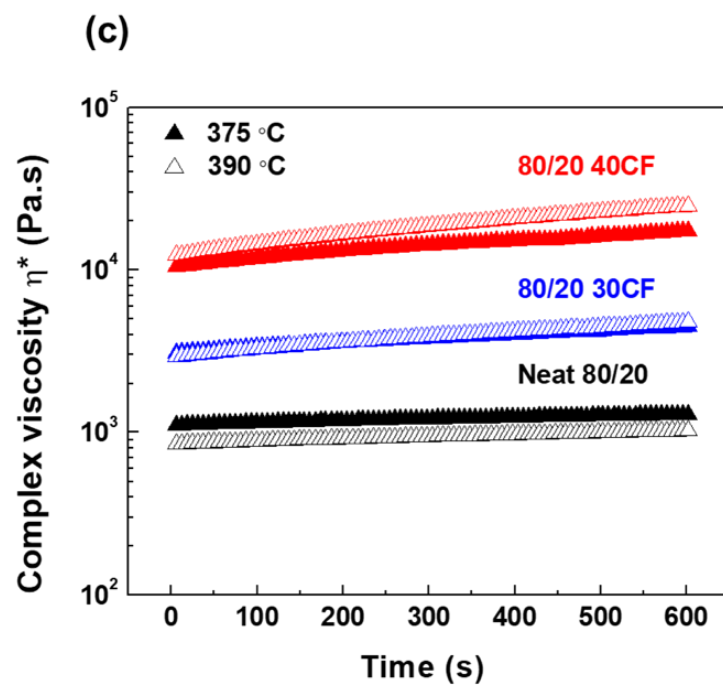


Figure 2.12 (continued).

Since the viscosity increase is notably faster and more significant for the filled grades, all the subsequent frequency sweep tests were conducted in nitrogen test environment. Based on this, the use of an inert cover gas in the extruder for systems like the BAAM is recommended during the processing of these materials.

Frequency Sweep Tests

Figure 2.13 (a-d) represents dynamic moduli and complex viscosity data for isothermal frequency sweep tests for the three neat PEKK grades. The plots indicate average values of these quantities obtained from frequency sweep tests from high-to-low range and vice versa. Note that standard deviations were low to be indicated on these plots (typically less than 10%). Figure 2.13 (a-c) indicates an increase in G' and G'' with frequency, as expected. For most polymer systems, at low frequencies, the test time is large enough and greater than the relaxation time of the polymer chains, giving rise to the possibility of the chains to recover to their original state under low strain conditions. As frequency increases, the test time shortens and the chains might not recover to their original state, thereby exhibiting greater stiffness⁷⁴. For all the three grades, we do not observe a crossover point (where $\tan \delta = G'' / G' = 1$) in the frequency range tested, indicating these unreinforced grades show primarily viscous behavior at all frequencies. The variation of complex viscosity with frequency (Figure 2.13 d) shows these neat grades to exhibit fairly Newtonian behavior at low frequencies and shear thinning behavior at frequencies greater than ~ 10 rad/s. Since the BAAM extrusion shear rate is expected to be in the range of $100\text{--}200\text{ s}^{-1}$, shear thinning in this range is beneficial to enable easier processing.

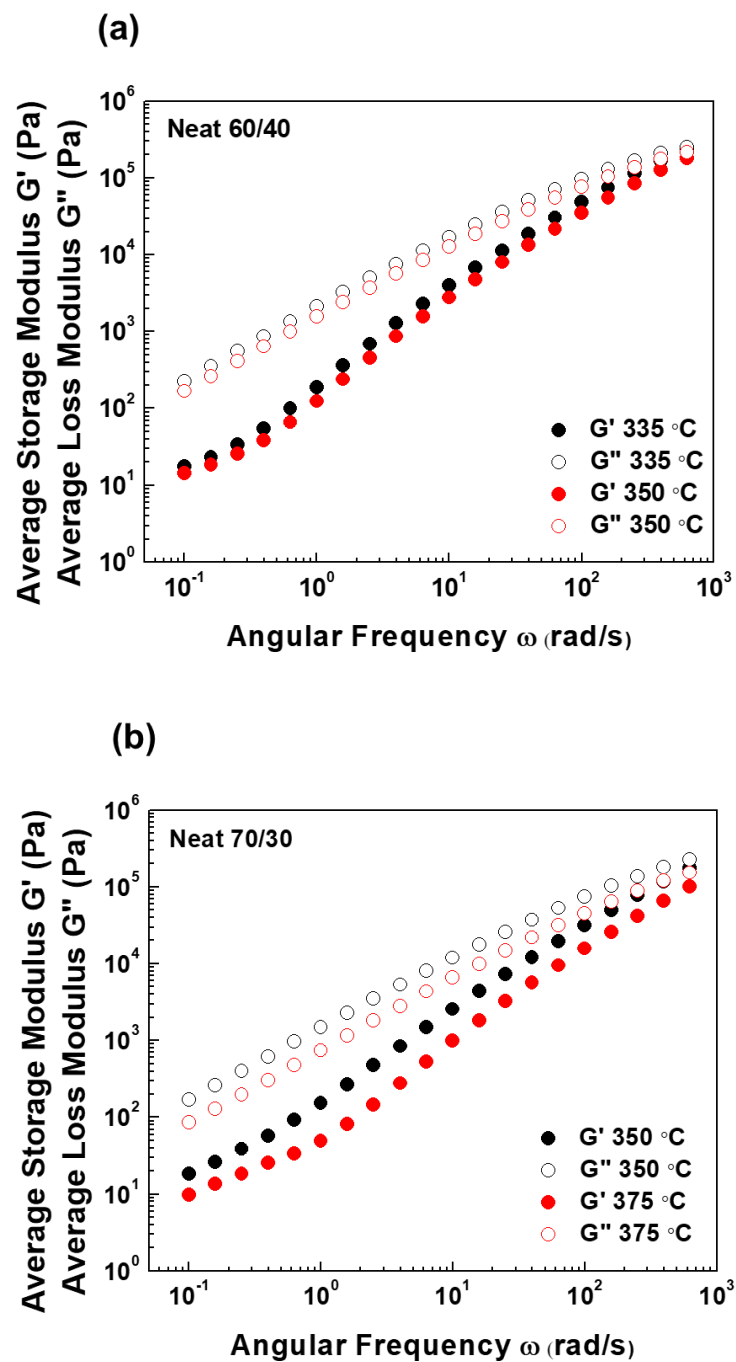


Figure 2.13 Frequency sweep tests for neat PEKK grades; Dynamic moduli for (a) 60/40, (b) 70/30, (c) 80/20; and (d) Complex viscosity for all three grades.

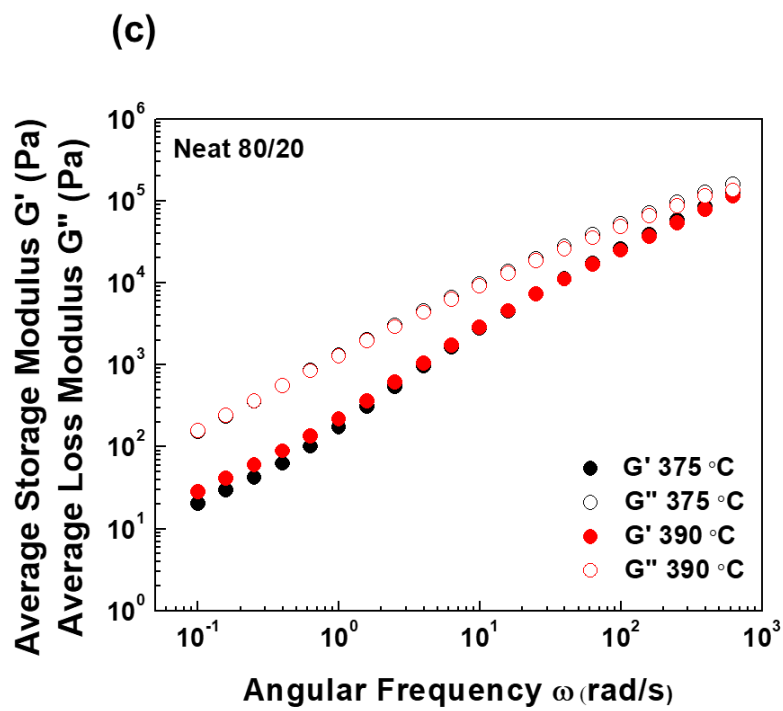
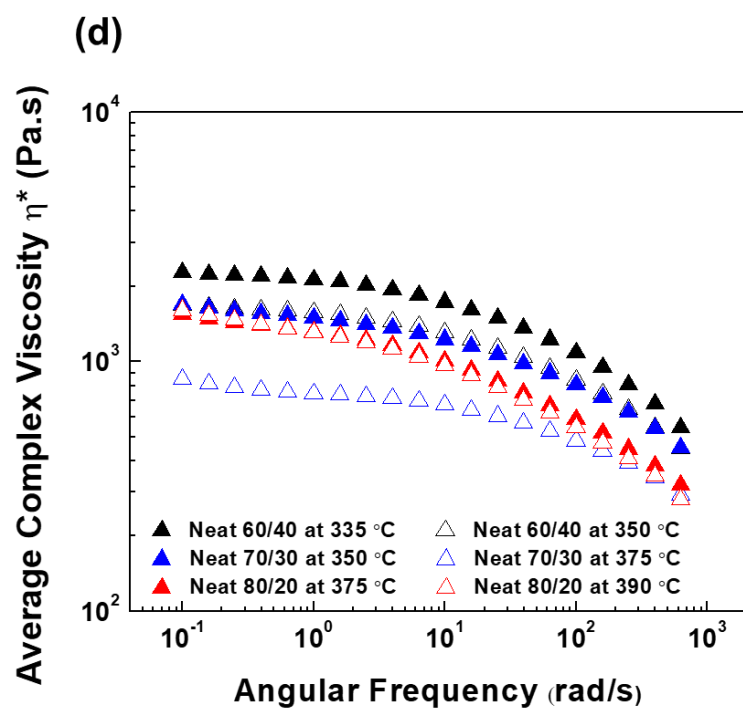


Figure 2.13 (continued).

Table 2.3 indicates the values of power law shear thinning exponent (n) calculated between 10- 628 rad/s (based on Equation 2.1)⁷³.

$$\eta = k (\dot{\gamma})^{n-1} \quad \text{Eq. (2.1)}$$

80/20 grade exhibits relatively slightly higher shear thinning than the other two grades. However, the effect of temperature has been observed to be least pronounced for 80/20 grade, whereas an increase in temperature has shown decrease in viscosity for 60/40 and 70/20 grades. In terms of setting processing conditions for AM, this behavior indicates that varying the shear rate by changing the extrusion screw speed (flow rate) may be a more effective method for altering the effective viscosity than changing temperature for the 80/20 grade.

The frequency sweep data for the three 80/20 grades (in nitrogen) at the two candidate test temperatures is represented in Figure 2.14 (a-c). Similar to the neat grades, both G' and G'' increase with increasing frequencies and also with increasing filler content. In addition, the crossover point shifts to lower frequencies with both increase in filler content and temperature, indicating an increase in elastic behavior and relaxation time with the addition of fillers. The complex viscosity data shown in Figure 2.14c indicates an increase in viscosity with the addition of fillers, as expected, since fillers obstruct the mobility of the polymer chain segments. However, this increase is greater at lower frequencies, an effect that has been observed for other filled systems such as CNTs in polycarbonate, glass fiber suspensions in LLDPE, and other polypropylene composites⁷⁴⁻⁷⁷. This can be explained in terms of the extent of movement of fillers with changing polymer viscosity (with changing shear rates).

Table 2.3 Power law shear thinning exponents for neat PEKK grades.

PEKK Grade	Temperature (°C)	Shear Thinning Exponent ‘n’
60/40	335	0.73
	350	0.75
70/30	350	0.76
	375	0.80
80/20	375	0.73
	390	0.71

For the SAOS tests, the fibers are randomly oriented since the pellets are melted between the parallel plates. At low shear rates (frequencies), although the deformation is low, the fibers tend to align along the flow direction but do not fully reorient. Since the viscosity of the matrix is higher at lower shear rates, the resistance to fiber movement is also greater, which gives rise to increased stress to maintain the same shear rate, thereby increasing viscosity. However, for AM processing, since shear rates are higher in the range of 100-200 s^{-1} , this behavior favors processing of even highly filled systems as the viscosities at the nozzle would not be as significantly affected by filler content. However, it should be noted that the zero shear viscosities of the filled systems would be higher and would need to be overcome to start initial flow of these materials during extrusion. This can be observed by the increased dependence of viscosity on filler concentration at lower frequencies (or shear rate), i.e., shift in Newtonian plateau to lower frequencies with increasing filler loading (although the plateau region is not observed in the frequency range of testing for filled grades). This would have to be overcome by sufficient driving pressure in the AM system used. In addition, the extent of shear thinning is also enhanced by the addition of fillers (lower shear thinning exponent 'n' observed with increasing filler loading, as shown in table 2.4). This behavior has been reported for other filled polymer systems as well, such as carbon nanofiber and glass fiber reinforced polyethylene composites^{74,78}. The effect of temperature on viscosity is not significant, especially for the filled grades across all frequencies, thereby enabling a wider processing window to be able to set the most suitable processing conditions when processing for AM applications.

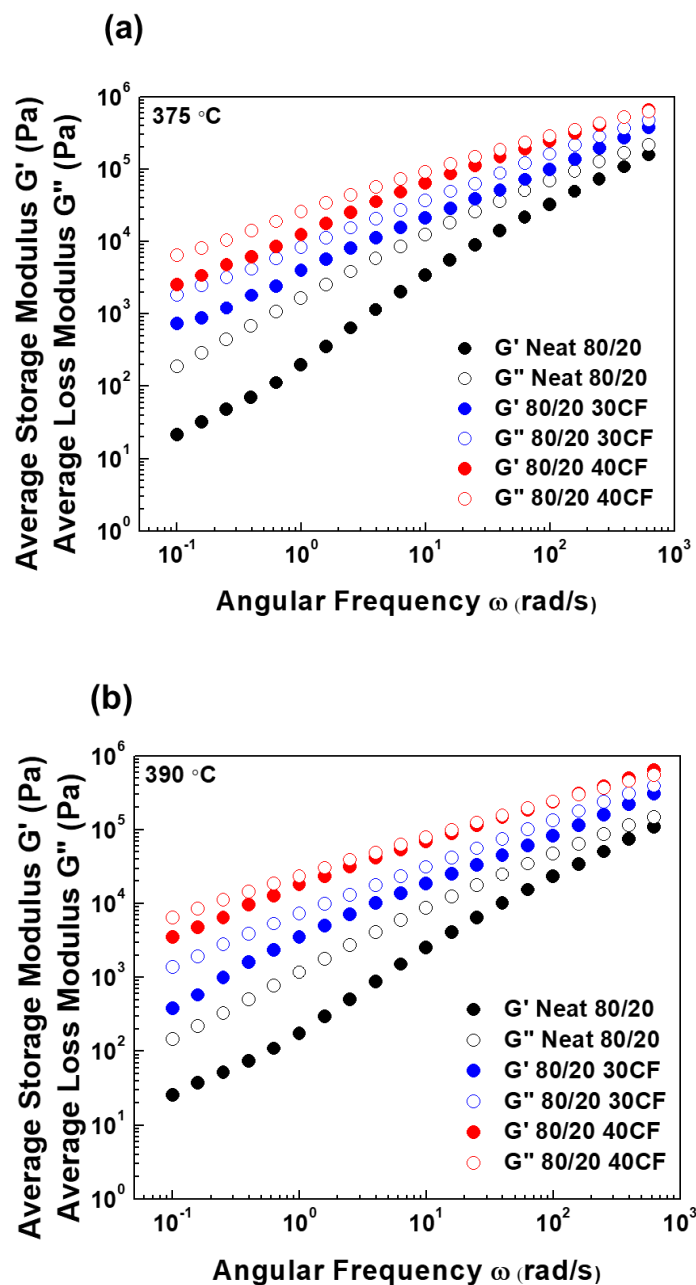


Figure 2.14 Frequency sweep tests for PEKK 80/20 grades; (a) Dynamic moduli at 375 °C, (b) Dynamic moduli 390 °C and (c) Complex viscosity at 375 °C and 390 °C.

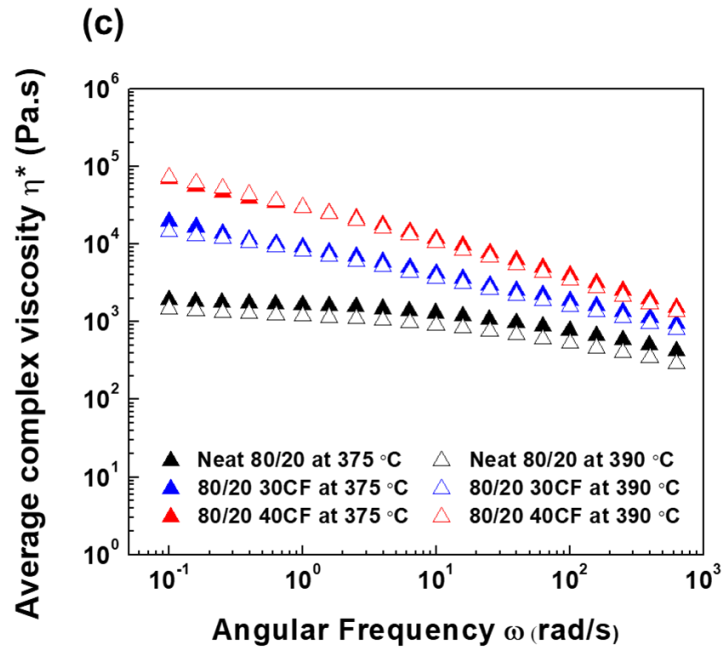


Figure 2.14 (continued).

Table 2.4 Power law shear thinning exponents for PEKK 80/20 grades.

80/20 Grade	Temperature (°C)	Shear Thinning Exponent 'n'
Neat	375	0.73
	390	0.73
30 wt.% CF	375	0.65
	390	0.64
40 wt.% CF	375	0.51
	390	0.50

Small Amplitude Oscillatory Shear (SAOS) Tests for PPS

Thermal Stability Tests

Figure 2.15 (a,b) represents the variation of dynamic moduli and viscosity with time in air for neat PPS pellets at the two lowest chosen temperatures (300 °C and 315 °C). Similar to neat PEKK grades, at both the temperatures, G'' is greater than G' , indicating the melt to be more viscous than elastic. Interestingly, although G'' lowers with an increase in temperature as expected, G' increases as the temperature increases. With respect to time, at 300 °C, there is no significant variation in complex viscosity or loss modulus, however, the storage modulus increases by about 2.5 times in 10 min. This is indicative of an increase in the elastic behavior of neat PPS with time, tending towards the possibility of crosslinking up on exposure to higher temperatures or for longer periods of time. The data at 315 °C in air clearly indicates an increase in complex viscosity, as well as dynamic moduli in 10 min in air. Viscosity increased by 45% and G' increased by almost an order of magnitude. This indicates the beginning of viscosity build up as the temperature increases, indicating structural changes happening to the material. This is further confirmed by the data in Figure 2.15b, which indicates the absence of viscosity build up in nitrogen at 315 °C unlike in air, which is indicative of an oxidative reaction in the melt that could be causing the structural change. Hence, all the subsequent tests for neat as well as carbon fiber reinforced PPS, have been performed in a nitrogen environment. This is because the sizing present on the surface of CF in the filled grades can degrade at the melt temperatures and add to the possibility of accelerating crosslinking.

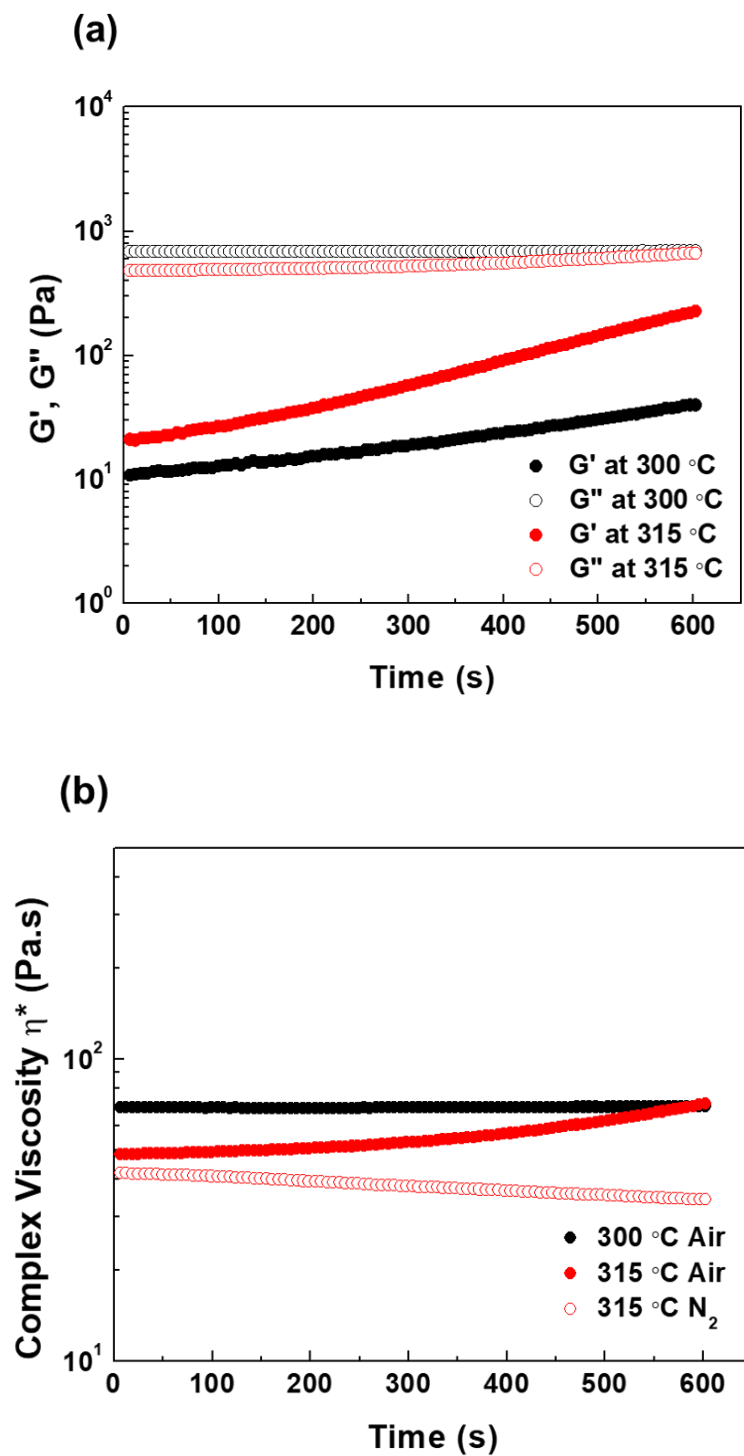


Figure 2.15 Variation of (a) Dynamic moduli in air, and (b) Complex viscosity (air and nitrogen) with time for neat PPS.

Frequency Sweep Tests

Figure 2.16 represents frequency sweep tests for neat, PPS 40CF and PPS 50CF grades at some of the chosen candidate temperatures. It should be noted that the data represented here is not at every chosen temperature, especially for the filled grades, since the high filler content and test temperatures made it difficult to obtain consistent, noise free data. The data shown in Figure 2.16 (within 20% variation based on multiple tests with fresh samples) still helps to determine the range in which the dynamic moduli and complex viscosity for these materials lie and their shear thinning behavior due to the addition of fillers.

From the frequency sweep tests, it is evident that the viscosity increases with the addition of fillers across all frequencies, along with the increase in the extent of shear thinning, as expected and similar to the effect observed for PEKK. Also, the effect of temperature is relatively more prominent for the neat grade and minimizes with the addition of CF. Similar to PEKK, to process filled grades of PPS, varying the shear rate at the nozzle could be a better way to control flow properties than varying the temperature.

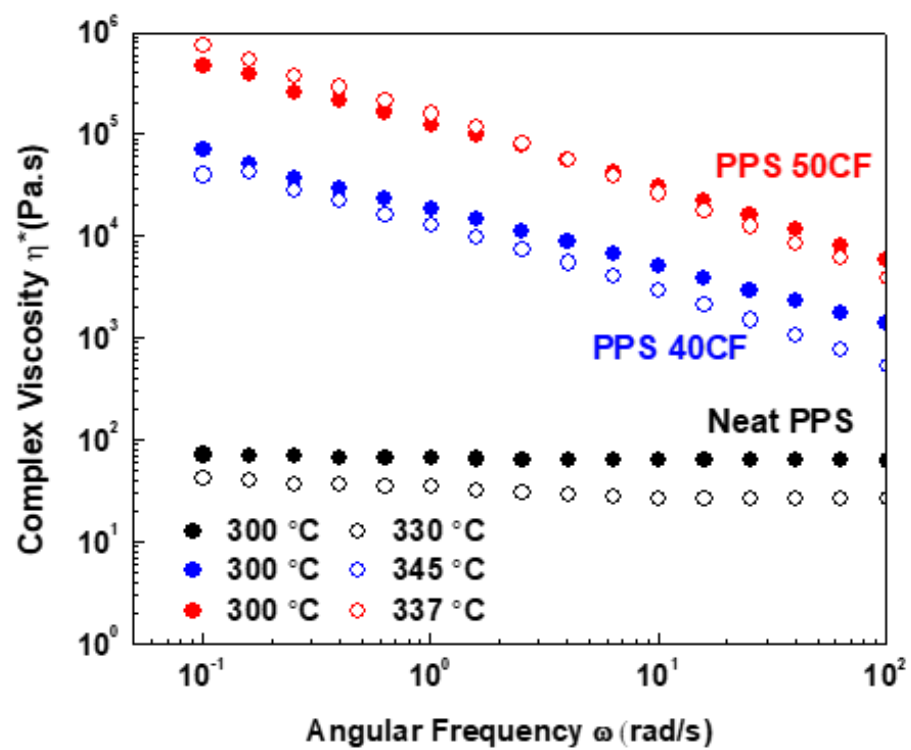


Figure 2.16 Frequency sweep tests for PPS grades at their candidate test temperatures.

Steady Shear Tests for PEKK

Figure 2.17(a-c) represents the variation of apparent shear viscosity with apparent shear rate for all the five grades of PEKK tested using a die with $L/D = 20$ at their candidate test temperatures. It can be observed that all the three neat grades shear thin, showing the same trend observed in SAOS tests. For the reinforced systems (Figure 2.18), increasing filler loading increases shear viscosity and the effect of filler loading on viscosity is less significant at higher shear rates (similar behavior was observed during SAOS tests). This can be attributed to the orientation of polymer chains and fillers in the flow direction at such high deformation rates, which lowers the viscosity.

Steady Shear Tests for PPS

Figure 2.19 represents steady shear tests for the three PPS grades performed on the capillary rheometer. The data shows the variation of apparent shear viscosity with apparent shear rate at certain chosen temperatures. The low temperature data is not shown here for the filled grades owing to the difficulty in obtaining good data in the shear rate range considered as the initial force required to overcome the zero-shear viscosity of the material was too high for the load cell used. Also, for the neat grade, the viscosity was very low at higher temperatures to get noise free data. Similar to the trends observed for PEKK, all the three grades exhibit shear thinning, which increases with the filler content and the effect of filler loading reduces at high shear rates.

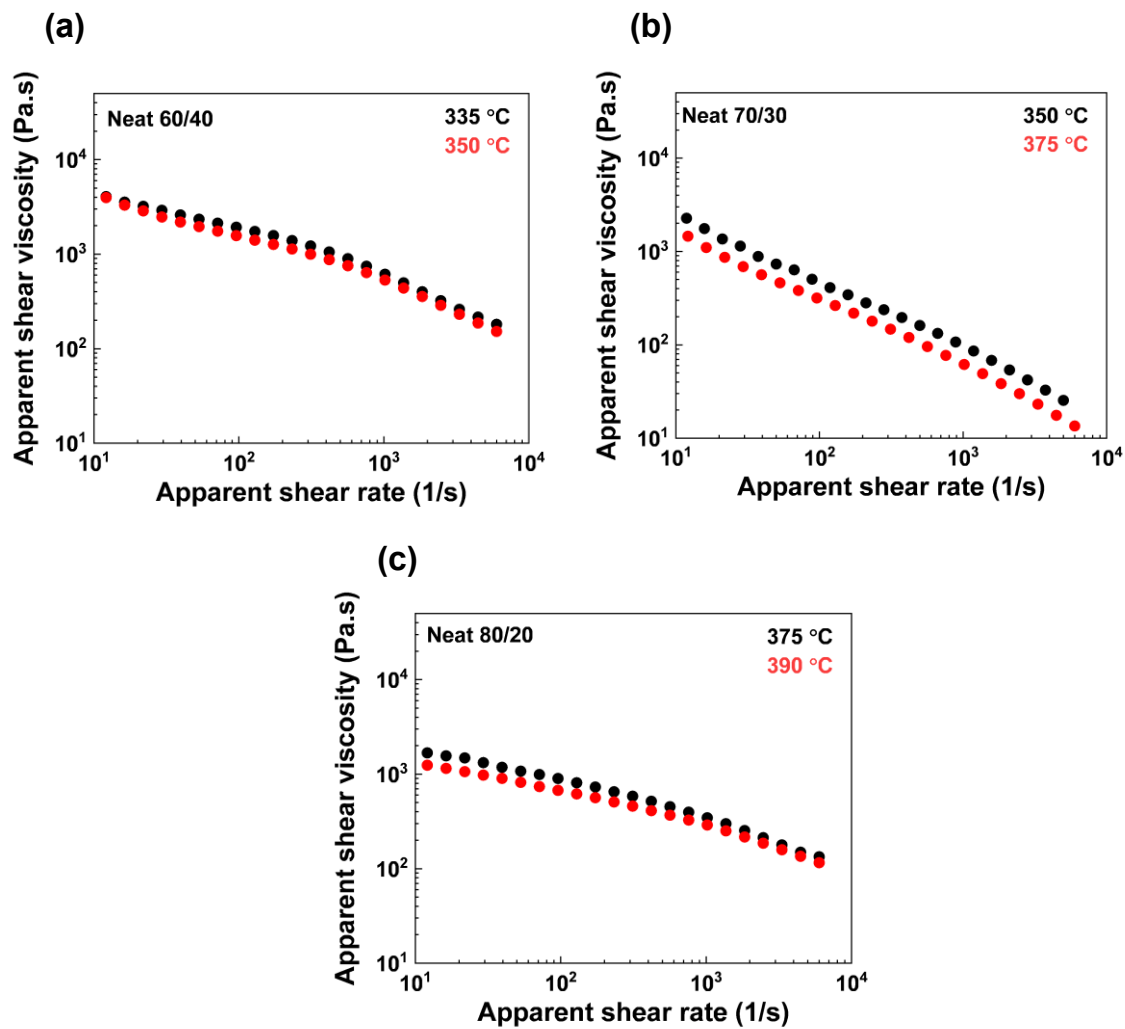


Figure 2.17 Variation of apparent shear viscosity with apparent shear rate for neat PEKK grades; (a) 60/40, (b) 70/30 and (c) 80/20.

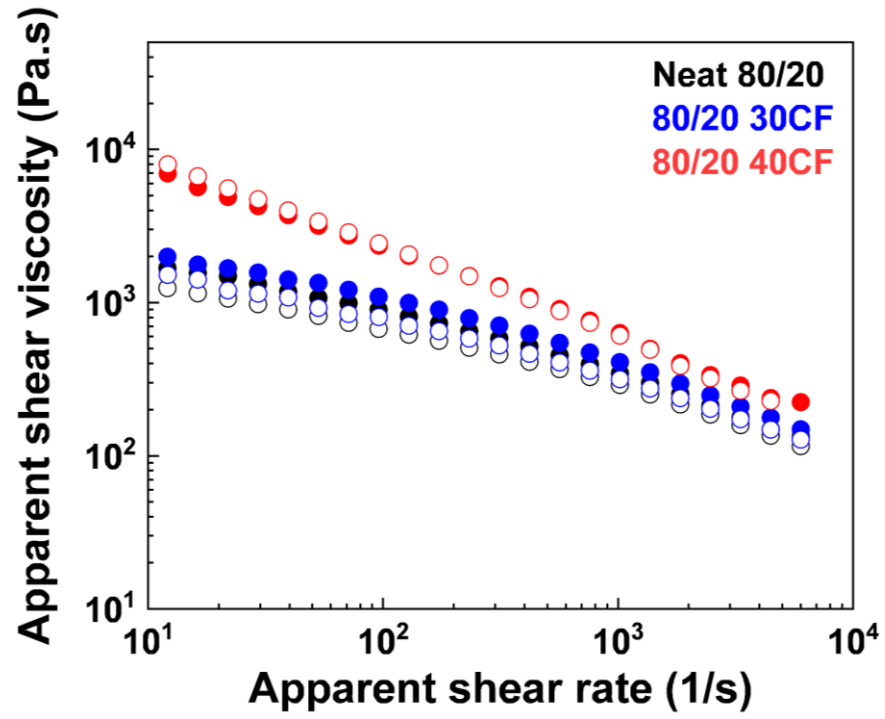


Figure 2.18 Variation of apparent shear viscosity with apparent shear rate for the three PEKK 80/20 grades.

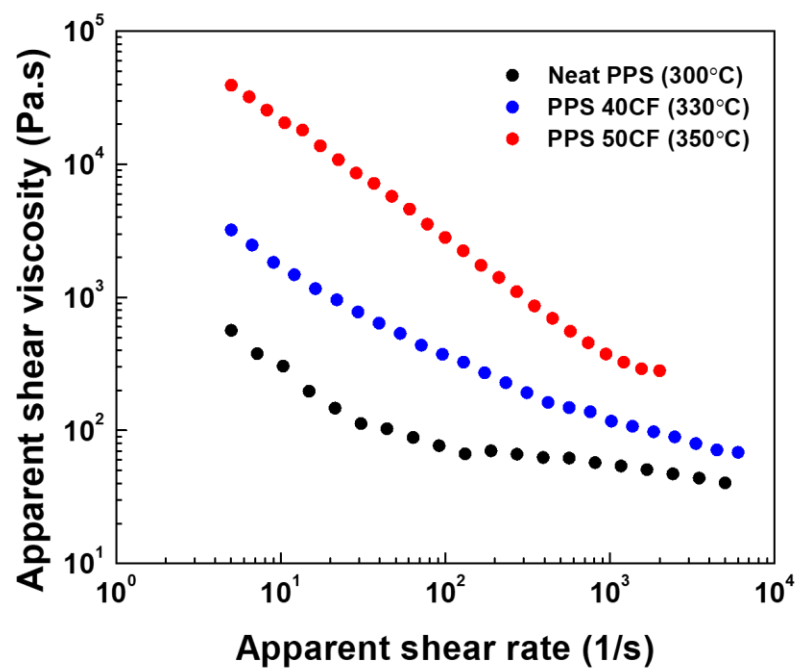


Figure 2.19 Variation of apparent shear viscosity with apparent shear rate for the three PPS grades at some chosen temperatures.

2.3.3. Extrusion on EDAM Platform

Print Trials on Fused Filament Fabrication (FFF) Platform

For the chosen grades of PEKK and PPS, filaments that could be used as feed material for FFF process were successfully extruded at temperatures (T_{ext}) and with diameters (d) as indicated in Figure 2.20. Extrusion through the nozzle on FFF platforms was possible for all the neat grades of PPS and PEKK at temperatures in the range identified from thermal and rheological analysis and nozzle sizes and print speed leading to shear rates in the range of $100 - 250 \text{ s}^{-1}$, which is typical for FFF process^{22, 79}. A few layers were printed as shown in Figure 2.21. Continuous print was limited by temperature fluctuations and printer hardware requirements. For the fiber reinforced grades of PPS and PEKK, although extrusion through the nozzle was possible initially, fiber clog issues and temperature fluctuations made it challenging to continue printing. Since CF reinforced grades are well suited for the BAAM process, print trials were performed on BAAM, as discussed in the following section.

PEKK 60/40  $T_{\text{ext}}: 335\text{ }^{\circ}\text{C}$ d: 1.5-1.75 mm	PEKK 70/30  $T_{\text{ext}}: 350\text{ }^{\circ}\text{C}$ d: 1.5-1.75 mm	PEKK 80/20  $T_{\text{ext}}: 370\text{ }^{\circ}\text{C}$ d: 1.5-1.75 mm	80/20 30CF  $T_{\text{ext}}: 375\text{ }^{\circ}\text{C}$ d: 1.6-1.9 mm	80/20 40CF  $T_{\text{ext}}: 375\text{ }^{\circ}\text{C}$ d: 1.5-1.9 mm
Neat PPS  $T_{\text{ext}}: 300\text{ }^{\circ}\text{C}$ d: 1.5-1.9 mm	PPS 40CF  $T_{\text{ext}}: 345\text{ }^{\circ}\text{C}$ d: 1.4-1.7 mm	PPS 50CF  $T_{\text{ext}}: 345\text{ }^{\circ}\text{C}$ d: 1.4-1.7 mm		

Figure 2.20 Filaments extruded for FFF (T_{ext} : filament extrusion temperature, d: filament diameter).

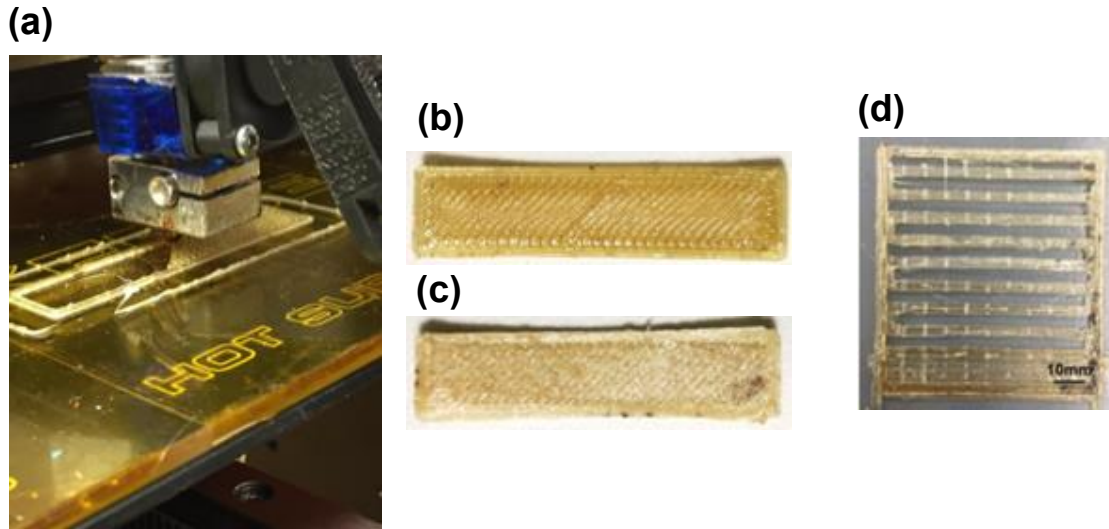
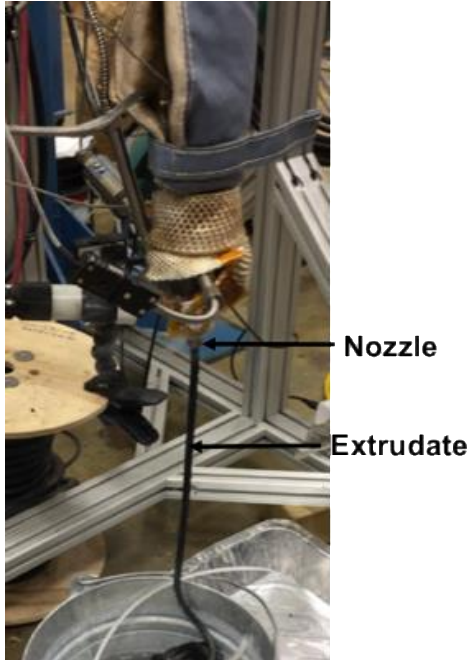


Figure 2.21 (a) FFF printing process; Sections printed using (b) PEKK Neat 60/40, (c) PEKK Neat 70/30 and (d) PEKK Neat 80/20.

Print Trials on the BAAM System

Carbon fiber reinforced grades of PPS (40CF and 50CF) and PEKK (80/20 40CF) were successfully extruded through the BAAM extruder set-up (Figure 2.22). The two PPS grades were extruded at temperatures in the range identified from thermal and rheological analysis in extruder with inert gas purge as recommended. Components (tools) were successfully printed using the two CF reinforced PPS grades⁶⁹. For the PEKK 80/20 40CF grade, extrusion of the material through the BAAM extruder set-up at temperatures and shear rates identified was possible⁷⁰.

(a)



(b)

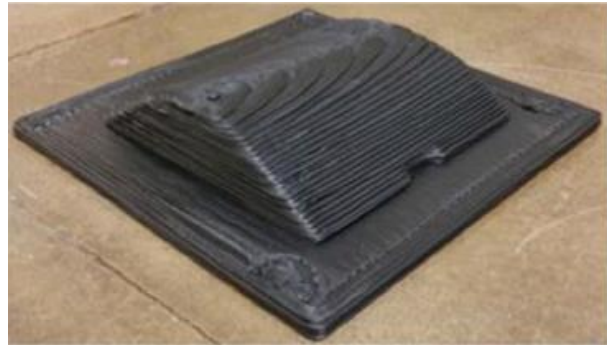


Figure 2.22 (a) Extrusion of PEKK 80/20 40CF (Kishore, V. et.al.⁷⁰) and (b) Tool printed using PPS 50CF (Hassen, A.A., et.al.⁶⁹).

2.4. Summary and Conclusions

This work focused on investigating different grades of neat and carbon fiber (CF) reinforced poly (ether ketone ketone) (PEKK) and polyphenylene sulfide (PPS) for extrusion deposition additive manufacturing. Six parameters, namely, temperature, time, shear rate (frequency), test environment, fillers and polymer structure were identified as key factors that influence rheological properties during processing. As the first step, thermal analysis was performed to define the processing temperature limits. Up on identifying a suitable temperature range, small amplitude oscillatory shear (SAOS) tests were performed to determine effect of time, temperature, tests environment and frequency

on the dynamic moduli and viscosity of the chosen materials. This was followed by steady shear tests in a capillary rheometer, accounting for orientation during flow, which is more replicative of the extrusion process. Finally, based on the processing temperature, environment identified from rheological analysis and nozzle shear rates in the range of 100 to 250 s⁻¹, extrusion deposition trials were performed on both small-scale printer as well as on the BAAM system for the carbon fiber reinforced grades.

Overall, rheological characterization was useful to identify suitable processing conditions and make recommendations for processing high temperature materials such as PEKK and PPS composites. Thermal and rheological analysis primarily indicated:

- (i) Neat grades of PEKK to be more stable in air than the fiber reinforced grades and neat PPS to be stable in air (at lower temperatures) than the fiber reinforced grades.
- (ii) Increase in temperature increased the viscosity build up for all the filled grades of PEKK and PPS with time, with the effect increasing with increasing filler loading. This indicated reduced thermal stability due to possible crosslinking taking place at higher temperatures.
- (iii) Addition of CF fillers increased the dynamic moduli, viscosity, as well as enhanced the shear thinning behavior for both PEKK and PPS.
- (iv) The effect of temperature on viscosity was less pronounced for the filled grades of PEKK and PPS.

For processing CF filled PPS and PEKK on large-scale BAAM system,

- (iv) Use of inert atmosphere (cover gas) is recommended while processing filled grades of PEKK and PPS to minimize viscosity build-up.
- (v) Since the effect of variations in shear rate on viscosity is greater than the effect of changes in temperature for all the filled grades, changing shear rate by varying the nozzle size or screw speed could be a better way of altering melt flow properties at the nozzle than changing the temperature.

3. Post-Processing Annealing of Printed Components

3.1. Background

Mechanical properties of components made from semi-crystalline polymers are not just dependent on the polymer structure but also on the crystallinity of the final part. Isothermal annealing above the glass transition temperature (T_g) of the polymer and below its melting point (T_m) has been used as one of the methods for improving part crystallinity for molded components to enhance mechanical properties^{34, 44, 80}. Annealing at temperatures well above the T_g leads to greater polymer chain mobility, thereby allowing the molecules to arrange themselves to increase crystallinity⁸¹. Crystallization parameters that can influence mechanical properties include degree of crystallinity (X_c), crystallite structure, crystal perfection, size distribution, etc.^{30, 36}. Some studies on semi-crystalline polymers such as poly (ether ether ketone) (PEEK) indicated lower crystallinity to manifest as lower matrix modulus and compression strength but increased toughness, but in cases with the presence of large spherulites, toughness decreased³⁰. For PEEK composites with fillers, annealing increased the degree of crystallinity, thereby increasing tensile strength and modulus but lowered fracture energy. In the case of polyphenylene sulfide (PPS), annealing at temperatures between T_g and T_m can also be accompanied by solid state curing or crosslinking reactions^{45-46, 48, 52, 82}. Crosslinking reactions in PPS are thermal and oxidative, with the extent of crosslinking increasing with increasing annealing temperature^{43, 47}.

Annealing PPS has been used as a method to increase crystallinity in injection molded components. Previous studies on annealing PPS have shown that annealing

quenched PPS at temperatures in the range of 200 °C for times as low as 2 hr increased the crystallinity index, thereby leading to increased flexural modulus, dimensional stability, and density⁴⁴. In another study, annealing slightly crosslinked PPS at 204 °C (for 1 hr) increased flexural modulus, heat distortion temperature, heat of fusion, and density, which were once again found to be manifestations of crystallinity changes in the polymer network⁸¹. A majority of the studies reported in literature for PPS involving the effect of annealing on structure formation and mechanical properties are on grades with very low initial crystallinity (or amorphous state obtained by quenching)⁸¹ wherein the effect of parameters such as annealing time and temperature have been studied. In general, annealing temperatures that have been used in several studies range from 130 to 250 °C and annealing times have varied from 5 min to 7 days^{34, 43, 46, 83}. The choice of processing conditions is highly dependent on the grade of PPS used as well as the processing and application requirements.

For EDAM process, since crystallization of the printed layers occur non-isothermally, it is of interest in this work to determine the effect of annealing on partially crystalline samples. In addition, with the possibility of crosslinking, post-processing annealing of PPS at temperatures above T_g and below T_m can not only affect crystallinity but can also alter the chemical structure of the material, thereby influencing the mechanical properties.

This work investigates the effect of isothermal annealing technique on the mechanical properties of PPS composites printed on the large format EDAM system (BAAM system), also focusing on determining if crosslinking reactions occur and their

effect on crystallinity and mechanical properties. This chapter focuses on the characterization of four different grades of PPS; unreinforced (neat) PPS, and short carbon fiber reinforced grades with three different filler loadings (40 wt.%, 50 wt.% and 60 wt.%).

Primary Research Questions

The overall objective of this section can be divided into two parts:

- (i) Does isothermal annealing have an effect on the mechanical properties of components printed using short carbon fiber reinforced PPS on large format EDAM system?
- (ii) If there is an effect, which mechanism dominates, occurrence of crosslinking or changes in crystallinity?

3.2. Materials and Characterization

3.2.1. Materials

Four grades of PPS have been used in this study, unreinforced PPS (neat), PPS with 40 wt.% carbon fiber (PPS 40CF), PPS with 50 wt.% carbon fiber (PPS 50CF) and PPS with 60 wt.% carbon fiber (PPS 60CF), all obtained from Techmer PM, LLC in the form of pellets. Prior to all characterization and processing, the pellets were dried in an oven at 120 °C for 3 hr (neat) and at 130 °C for 4 hr (carbon fiber reinforced grades). Isothermal annealing was performed in a muffle furnace (KSL-1100X from MTI Corporation) at 250 °C in air.

3.2.2. Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) tests were performed on a Discovery Hybrid Rheometer (DHR-2) fitted with torsional DMA test geometry (Figure 3.1). Samples for DMA tests for the three carbon fiber reinforced grades were cut from larger sections (walls) printed on the Big Area Additive Manufacturing (BAAM) system. Samples were obtained in two orientations, x-direction (parallel to print direction) as well as z-direction (perpendicular to the print direction) as shown in Figure 3.2, with dimensions of 60 mm X 12 mm X 3mm. For neat PPS, DMA samples cut-off from injection molded disks (diameter: 62.5 mm, thickness: 3 mm) have been used.

Firstly, to identify the longest heat treatment time up to which there is some variation in the modulus of the material, isothermal time sweep tests were performed on the untreated samples at 250 °C at 1 Hz frequency and 0.05 % strain in air for 48 hr. Up on identifying the heat treatment time, temperature ramp tests were performed on both, untreated as well as samples isothermally annealed in the furnace at 250 °C in air for the time identified from the time sweep test. Temperature ramp tests were done by heating the samples from 40 °C to 250 °C at the rate of 2 °C/min in nitrogen at a frequency of 1 Hz and 0.05% strain.



Figure 3.1 DMA test set-up.

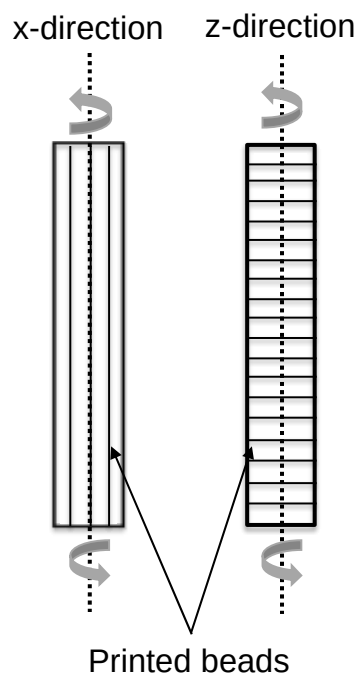


Figure 3.2 Sample orientation for DMA testing in torsion mode.

3.2.3. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) tests were performed on untreated as well as annealed pellets using TA Instruments Q2000 system. Pellets were broken down into smaller pieces and samples were prepared using about 5-7 mg of the pellets and T_{zero} aluminum pans and lids. Samples were heated from 25 °C to 350 °C at 10 °C/min, isothermally held at 350 °C for 2 min to erase any thermal history and cooled at 10 °C/min back to 25 °C, followed by another heating cycle up to 350 °C at 10 °C/min. All the three cycles were run in nitrogen environment to minimize degradation during the DSC scans.

3.2.4. Melt Rheology

Melt rheological analysis was performed on Discovery Hybrid Rheometer (DHR- 2) system fitted with 25 mm aluminum parallel plates geometry. Untreated pellets and pellets annealed in the muffle furnace (in air) were melted between the plates using melt rings. Frequency sweep tests were performed at 337 °C in nitrogen using 0.05% strain.

3.2.5. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a Nicolet iS50 FT-IR system from Thermo Scientific using an Attenuated Total Reflectance (ATR) probe to observe any changes in functional groups up on annealing. Samples used for FTIR analysis were untreated and annealed PPS powder to ensure better contact with the probe. ATR scans (64 scans per sample) were performed for wavenumbers between 4000 cm⁻¹ and 500 cm⁻¹.

3.2.6. Optical Microscopy

Optical Microscopy was performed on Keyence VHX 5000 microscope for the injection molded neat PPS samples to observe any variation in color change due to annealing. Sample sectioning to observe the cross-section was performed on Buehler Isomet 1000 sectioning saw.

3.2.7. Vickers Microhardness

Vickers microhardness tests were performed using Wilson VH1202 instrument for samples embedded in epoxy mounts and polished. The indentations were with a load of 100 g and 15 s dwell time. Measurements were taken at five spots for each test condition and the average values have been reported. The measured spots were separated by a distance of at least 3 times the length of the diagonal of the indent.

3.3. Results and Discussion

3.3.1. Dynamic Mechanical Analysis

Determination of Annealing Time

The time for which the printed samples should be annealed for was determined by performing time sweep test on PPS 50CF at 250 °C. This grade of PPS was chosen as it is one of the primary grades of interest for tooling. Untreated sample was annealed at 250 °C for 48 hr, subjecting it to a very small oscillatory strain (0.05 %) at 1 Hz frequency and the variation in storage modulus (G') was monitored. Figure 3.3 represents the time evolution of the dynamic moduli of PPS 50CF x-direction sample. An increase in G' is observed,

which is about 65% in the first 16-18 hr. Beyond that, the increase in G' is only marginal. Increase in G' at temperatures above T_g indicates an increase in the elastic behavior of the material, which could potentially arise from crystallization effects or from mechanisms such as crosslinking taking place. For subsequent tests to further investigate the possible mechanisms, 18 hr was selected as the annealing time. Although this time was chosen from tests on one grade of PPS with a certain thermal history acquired from printing process, this still served as a good starting point for further investigation.

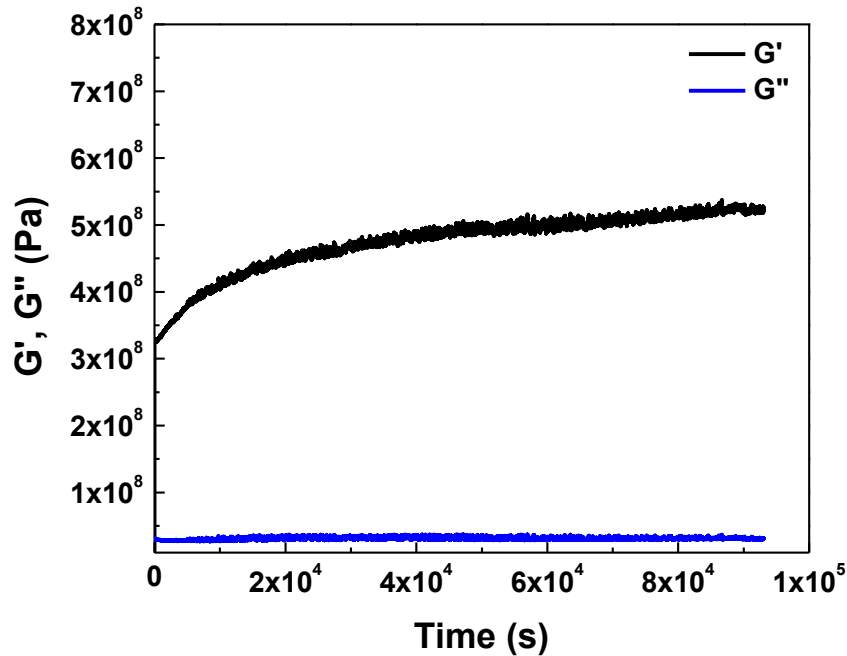


**Figure 3.3 Time evolution of dynamic moduli of PPS 50CF (x-direction) at 250 °C
(Tested at 1 Hz and 0.05% strain).**

Effect of Annealing on Mechanical Properties of PPS

Neat PPS

Figure 3.4 (a,b) represents the variation of storage modulus (G') and $\tan \delta$ with temperature for untreated and annealed (at 250 °C for 18hr in air) neat PPS samples (injection molded). From this data, it can be observed that the effect of annealing on G' is more prominent at temperatures above the glass transition temperature (T_g) of ~ 93 °C (calculated based on the onset of drop in G'). The increase in G' due to annealing is greater as the temperature increases. G' increased by 83% at 175 °C and by 149% at 250 °C (values as shown in Table 3.1). Such behavior in the increase of storage modulus above the material's T_g is typically indicative of an increase in constraints imposed by crystalline domains. Annealing also caused a small increase in the T_g by 4.3°C. For semi-crystalline polymers, an increase in T_g again, typically indicates increased crystallinity percent in the material⁸⁴. In the case of variation of $\tan \delta$ with temperature (Figure 3.4b), annealing lowered $\tan \delta$ overall across the entire temperature range tested, indicating a more elastic behavior of the material after heat treatment. Based on this data, for neat PPS, it can be observed that annealing overall improved modulus at temperatures above the T_g of the material. However, further tests have been performed to further investigate if changes in crystallinity is the primary dominating mechanism for changes in mechanical properties since increase in crosslinking could also lead to increased elastic behavior in the temperature range under consideration.

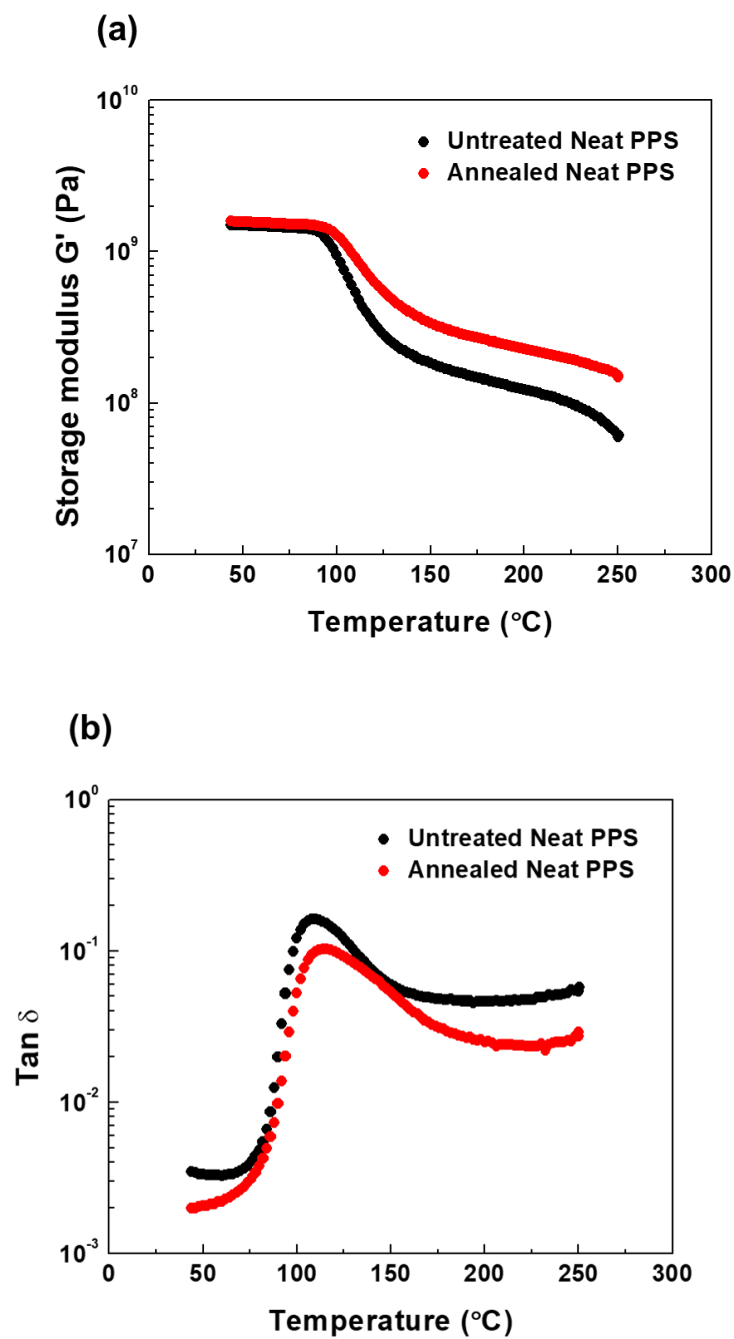


Figure 3.4 Effect of annealing on (a) Storage modulus and (b) $\tan \delta$ of neat PPS.

Table 3.1 Variation of G' with temperature for neat PPS.

Post-processing condition	T_g (°C) (G' onset)	G' at 50 °C (GPa)	G' at 175 °C (GPa)	G' at 250 °C (GPa)
None	93.23	1.491	0.146	0.061
18 hr, 250 °C, Air	97.54	1.572	0.267	0.152

Reinforced PPS

Effect of Sample Orientation

Figure 3.5 (a,b) shows the effect of sample (bead) orientation on G' and $\tan \delta$ for BAAM printed PPS 40CF samples. There is no significant difference in G' at temperatures below T_g for x-direction and z-direction samples. However, at temperatures above T_g , x-direction samples show a slightly higher G' (26 % greater at 175 °C and 25 % greater at 250 °C) than the z-direction samples. Tan delta peaks also overlap above T_g and there no variation in T_g based on sample orientation.

Effect of Annealing

Figure 3.6 (a-d), Figure 3.7 (a,b) and Figure 3.8 (a,b) represent the effect of annealing on variation of storage modulus and $\tan \delta$ with temperature for PPS 40CF, 50CF and 60CF respectively. Similar to the behavior observed for neat PPS, variation in G' was minimal at temperatures below T_g in most cases. However, above T_g , annealing increased G' , with the effect being greater as the temperature increased (shown in Table 3.2, Table 3.3 and Table 3.4). This can again be attributed to the possibility of increased crystallinity in the sample which restrict the movement of amorphous chains at temperatures above T_g . However, further investigation of the possible dominating mechanism has been discussed in the following sections.

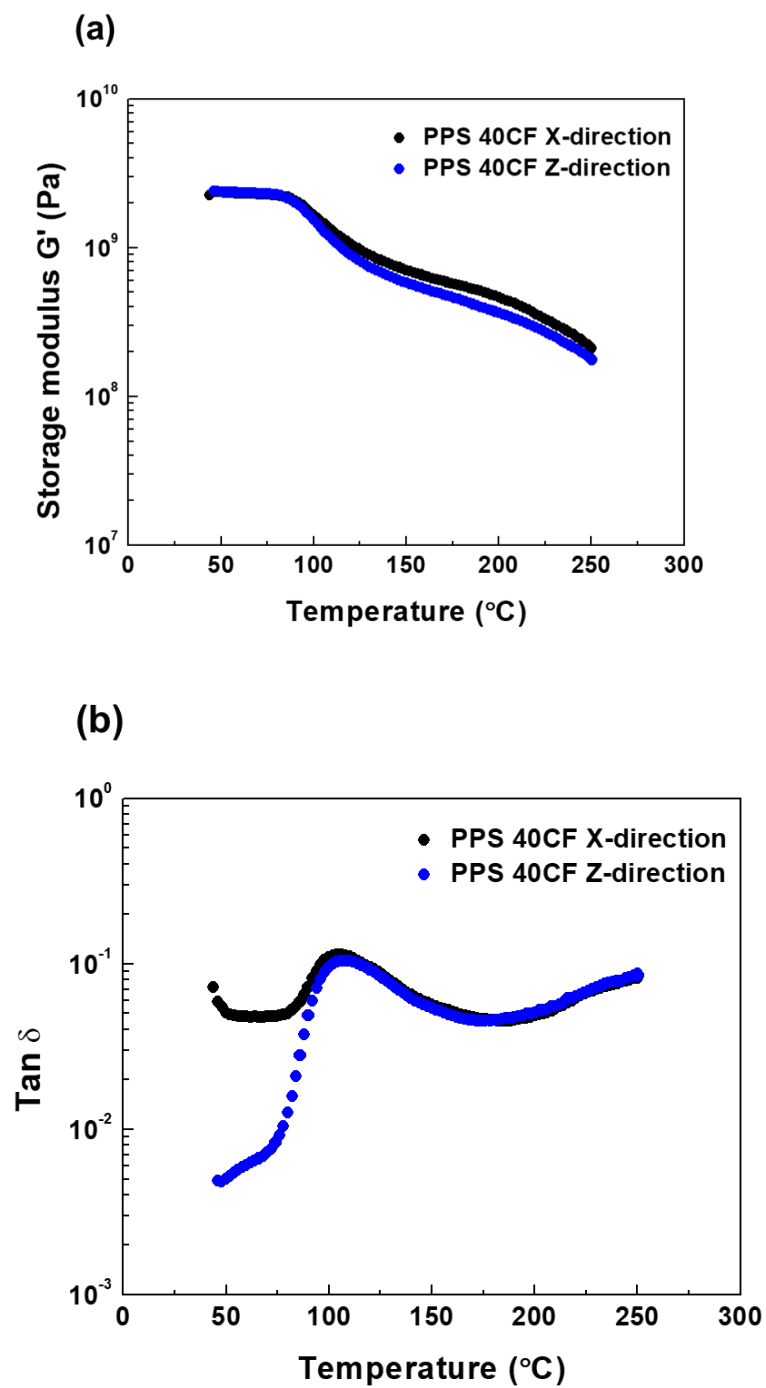


Figure 3.5 Effect of printed sample orientation on (a) Storage modulus and (b) $\tan \delta$ of PPS 40CF.

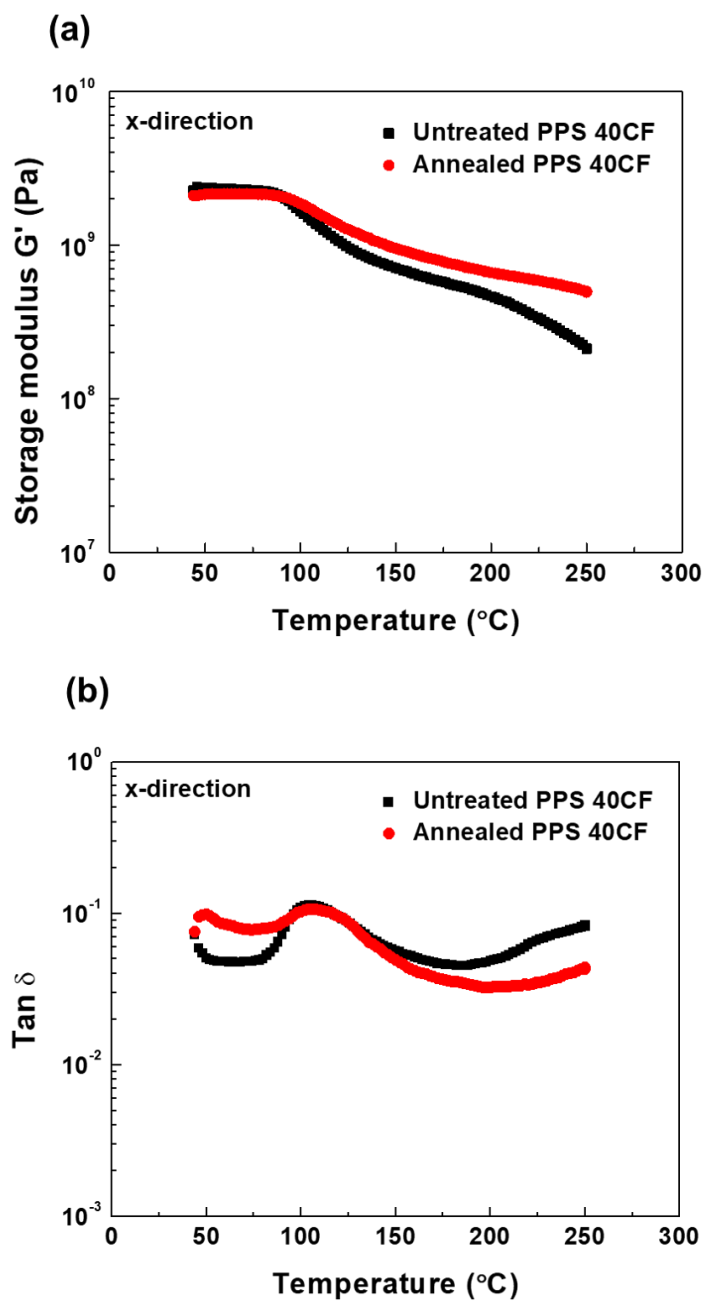


Figure 3.6 Effect of annealing on (a) Storage modulus (x-direction), (b) $\tan \delta$ (x-direction), (c) Storage modulus (z-direction), and (d) $\tan \delta$ (z-direction) of PPS 40CF.

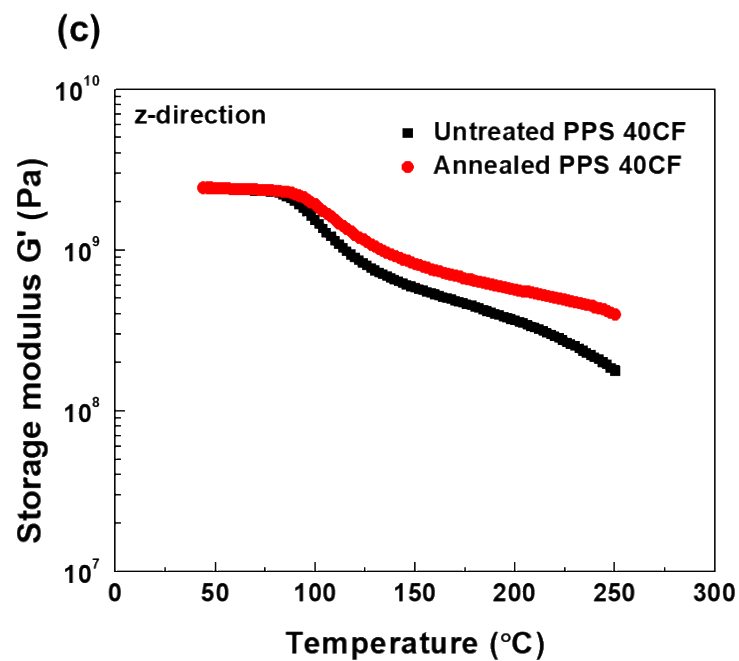
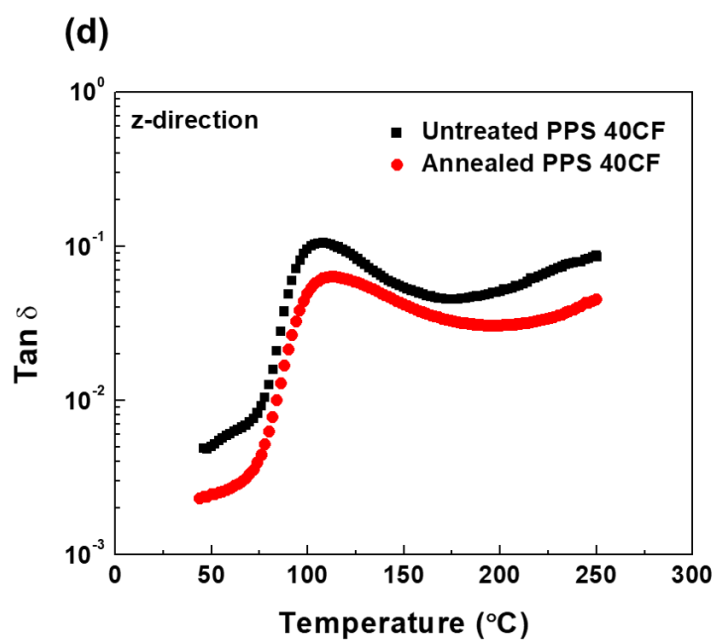


Figure 3.6 (continued).

Table 3.2 Variation of G' with temperature for PPS 40CF.

Post-processing condition		T_g (°C)	G' at 50 °C (GPa)	G' at 175 °C (GPa)	G' at 250 °C (GPa)
x-direction	None	89.12	2.460	0.552	0.222
	18hr, 250 °C, Air	93.16	2.150	0.771	0.490
z-direction	None	87.15	2.380	0.468	0.178
	18hr, 250 °C, Air	91.35	2.431	0.664	0.399

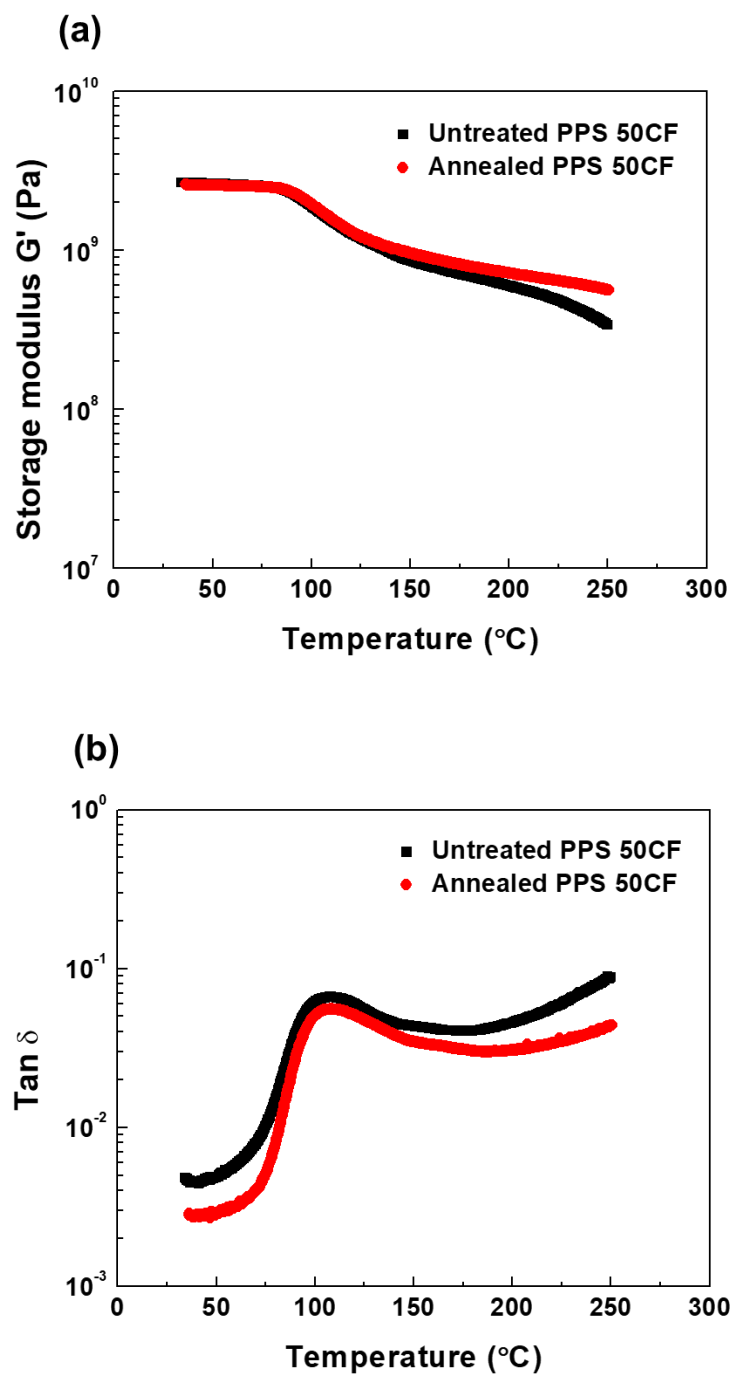


Figure 3.7 Effect of annealing on (a) Storage modulus and (b) $\tan \delta$ of PPS 50CF (x- direction).

Table 3.3 Variation of G' with temperature for PPS 50CF (x-direction).

Post-processing condition	T_g (°C)	G' at 50 °C (GPa)	G' at 175 °C (GPa)	G' at 250 °C (GPa)
None	86.17	2.613	0.706	0.345
18hr, 250 °C, Air	88.64	2.544	0.808	0.561

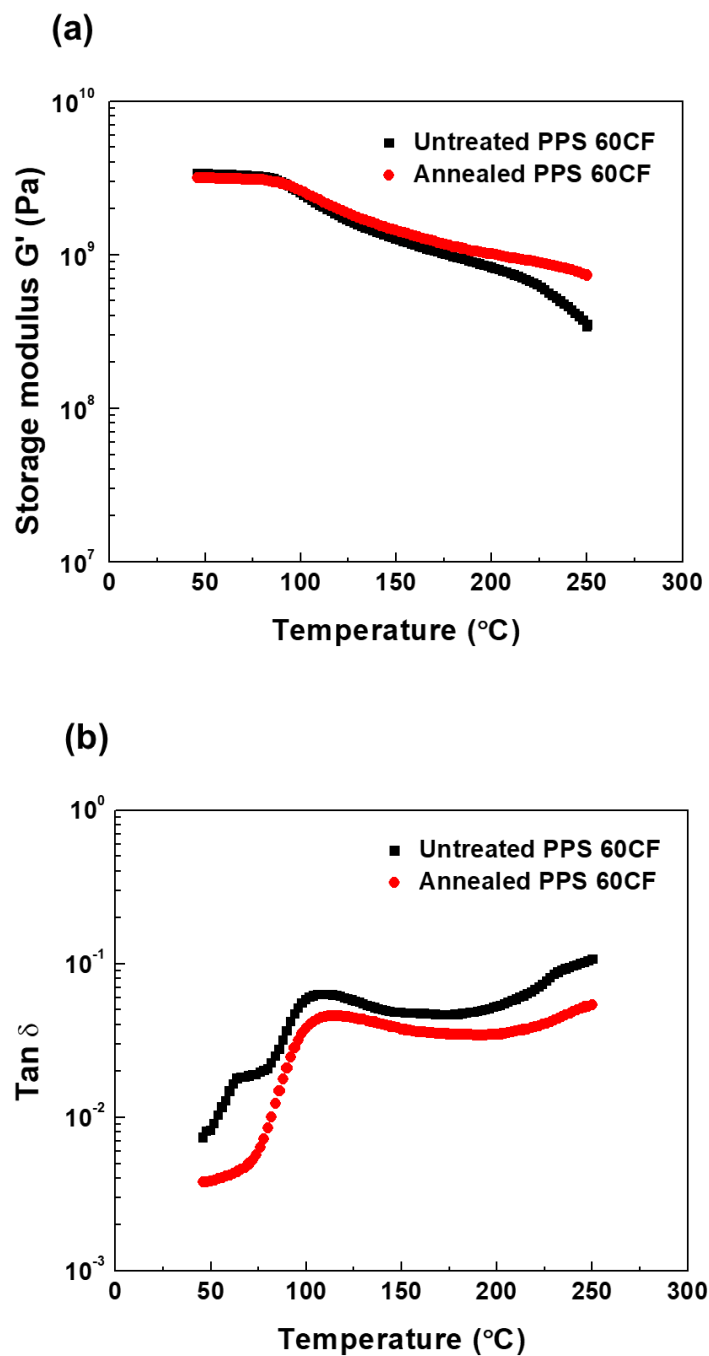


Figure 3.8 Effect of annealing on (a) Storage modulus and (b) $\tan \delta$ of PPS 60CF (x-direction).

Table 3.4 Variation of G' with temperature for PPS 60CF (x-direction).

Post-processing condition	T _g (°C)	G' at 150 °C (GPa)	G' at 175 °C (GPa)	G' at 250 °C (GPa)
None	86.22	3.365	1.003	0.339
18 hr, 250 °C, Air	88.87	3.158	1.167	0.729

3.3.2. Differential Scanning Calorimetry

Effect of annealing on crystallinity

Figure 3.9 (a-d) represents DSC thermograms of untreated and annealed pellets from the first heating cycle. The first heating cycle indicates changes in the material right after heat treatment. Table 3.5 summarizes the effect of annealing on changes in the degree of crystallinity. The degree of crystallinity for neat PPS was calculated using Equation 3.1 and that of the filled grades were calculated using Equation 3.2 (accounting for filler weight fraction)

$$X_c = \frac{\Delta H_f}{\Delta H_f^\circ} \quad (\text{Eq. 3.1})$$

$$X_c = \frac{\Delta H_f}{(1-W_f)\Delta H_f^\circ} \quad (\text{Eq. 3.2})$$

where ΔH_f is the heat of fusion obtained from first heating curve and ΔH_f° is the standard heat of fusion, taken to be 77.5 J/g⁶² and W_f is the weight fraction of the reinforcing fiber in the composite³⁴.

Overall for all grades, crystallinity increased up on annealing. The extent of increase was different for each grade, depending not only up on the effects of fillers but also on the thermal history imparted on the pellets during their production.

For neat PPS (Figure 3.9a), annealing led to an increase in the degree of crystallinity accompanied by the appearance of another new peak with a lower peak melting temperature (closer to the annealing temperature). This low melting peak could possibly correspond to newly formed crystals (of different size compared to the high melting crystals) due to annealing.

In the case of CF filled grades, similar trends were observed wherein new low melting peaks appeared (multiple peaks). This again indicated annealing to have given rise to the formation of low melting crystals of different sizes. In general, for the filled grades, the presence of CF alters crystallization in addition to the changes the matrix undergoes. Here, crystallization due to annealing can take place from the matrix, or on the surface of carbon fiber, thereby leading to multiple crystallite sizes, in addition to matrix modifications alone causing this effect³⁴.

From DSC analysis of first heating cycle, annealing for 18 hr at 250 °C in air indicated an overall increase in the degree of crystallinity for both neat as well as carbon fiber reinforced grades of PPS, which agrees well with the DMA analysis.

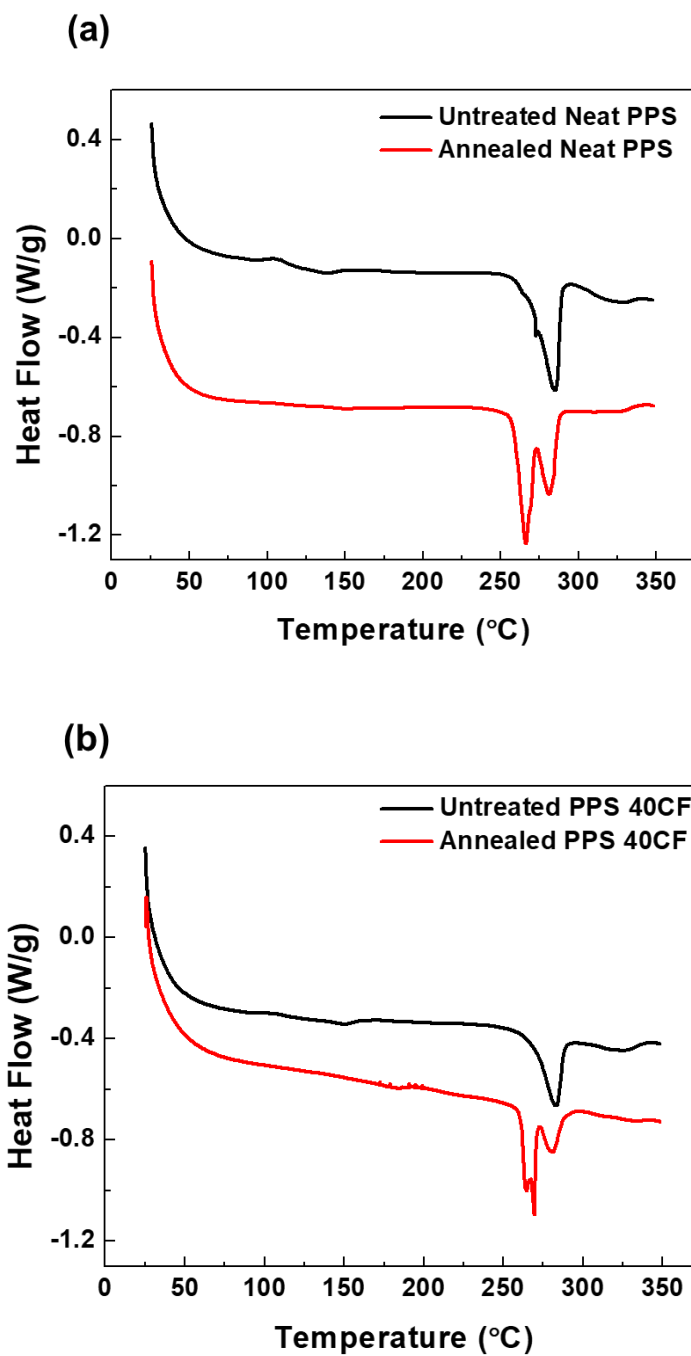


Figure 3.9 DSC analysis of 1st heating cycle for (a) Neat PPS, (b) PPS 40CF, (c) PPS 50CF and (d) PPS 60CF.

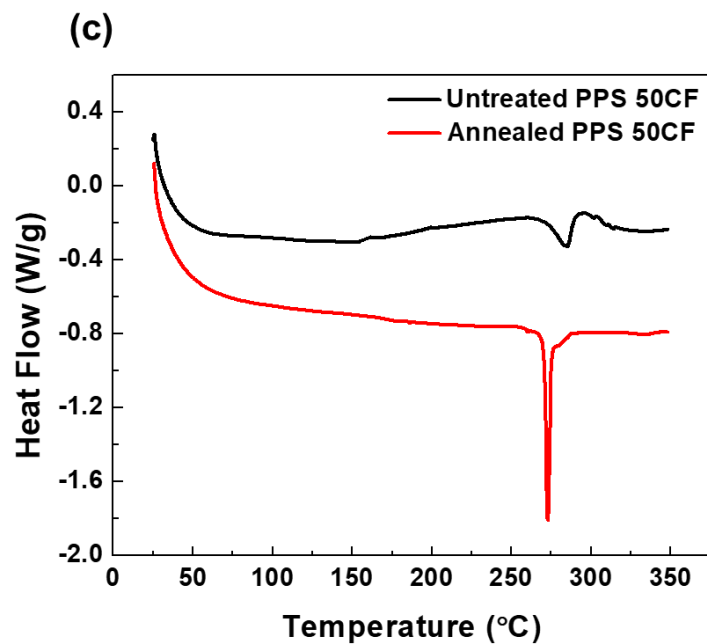
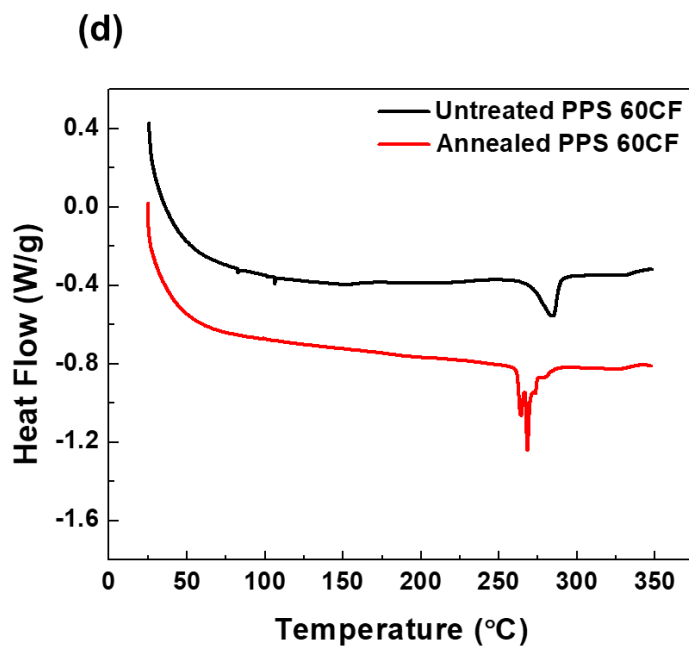


Figure 3.9 (continued).

Table 3.5 DSC analysis of untreated and annealed PPS pellets.

Material	ΔH_f (J/g) Untreated	ΔH_f (J/g) Annealed	X_c Untreated	X_c Annealed	Percent Increase in X_c
Neat PPS	37.34	51.66	0.48	0.67	39.6
PPS 40CF	20.43	31.16	0.43	0.67	55.8
PPS 50CF	12.44	24.69	0.32	0.63	96.9
PPS 60CF	16.04	19.13	0.52	0.62	19.2

Other effects due to annealing

The appearance of double peaks in the first melting endotherm of the as-annealed samples of neat PPS indicates possible structural change that could be taking place in the material in the form of branching, chain extension and slight crosslinking reactions which can give rise to the development of crystal domains of multiple sizes.

Supporting this possibility, visual observations of the samples, both pellets as well as molded specimens (as shown in Figure 3.10) indicated a color change (from pale white to brown) up on annealing. This is indicative of oxidation taking place in the material due to annealing in air since the change in color from white to brown deepened with annealing time (not shown here). To further study this effect, cooling curves from the DSC thermograms (for pellets) were analyzed to investigate possible structural changes taking place due to annealing. In the DSC tests, after the first heating cycle, the samples were melted above T_m (350 °C) and held at that temperature for 2 min (all in nitrogen) to erase thermal history.

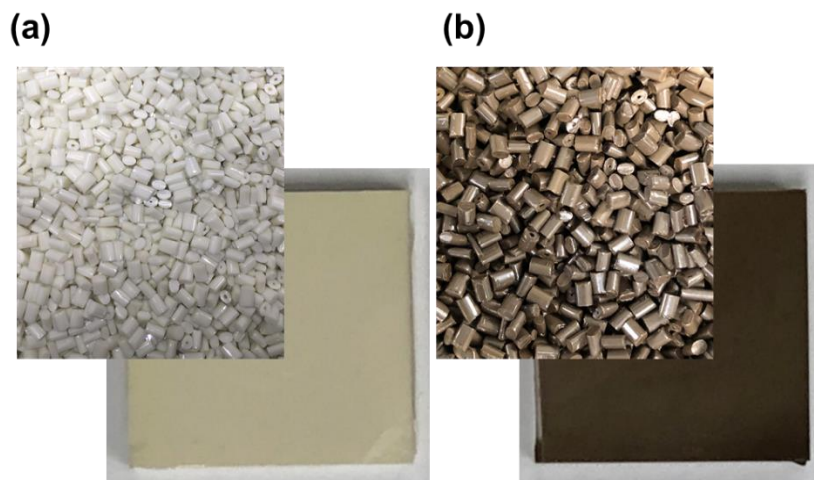


Figure 3.10 Neat PPS samples (a) Untreated and (b) Annealed.

This process would have erased all crystallinity changes that took place in the sample due to annealing as well as prior processing. When the samples (untreated and annealed pellets) are cooled from melt at a constant rate, any changes in their crystallization behavior would be primarily due to the structural changes taken place during annealing. Figure 3.11 (a-d) shows the cooling cycle data for the four grades of PPS.

Neat PPS

For neat PPS, annealed samples showed a higher crystallization onset temperature (T_{onset}) and peak crystallization temperature (T_c) when compared to the untreated samples (Figure 3.11a). This indicated an increase in crystallizability of the polymer from melt. This can be attributed to the introduction of new nucleating sites in neat PPS by the structural change taking place in the form of chain branching or slight crosslinking due to annealing⁴⁶. Also, there was a small reduction in the enthalpy of crystallization (ΔH_c) (as shown in table 3.6). Overall, this effect on the crystallization parameters due to annealing

indicate the possible occurrence of structural changes after isothermal heat treatment of neat PPS, which promotes crystallization at 250 °C.

CF Filled PPS

For CF filled grades of PPS, the re-crystallization exotherms from the cooling curve (Figure 3.11 b-d) indicated a trend opposite to that observed for neat PPS. Annealing shifted the T_{onset} and T_c to lower temperatures, indicating reduced crystallizability. This can be attributed to the presence of branching or some crosslinks which further restrict chain mobility in already highly reinforced matrices⁴⁶. For all the three grades of filled PPS, untreated samples have almost the same T_{onset} and T_c . However, after annealing, T_{onset} and T_c shift to lower temperatures with increasing fiber loading, indicating crystallinity to be more difficult as fiber loading increases. This effect can be due to effects of reduced polymer content in the composite as the filler loading increases, more sizing (and degradation of sizing taking place) present as filler loading increases, thereby accelerating branching and crosslinking reactions, and hindering crystallization. Overall, analysis of cooling cycles from DSC tests indicate structural changes taking place in all four PPS grades up on annealing which influence crystallization.

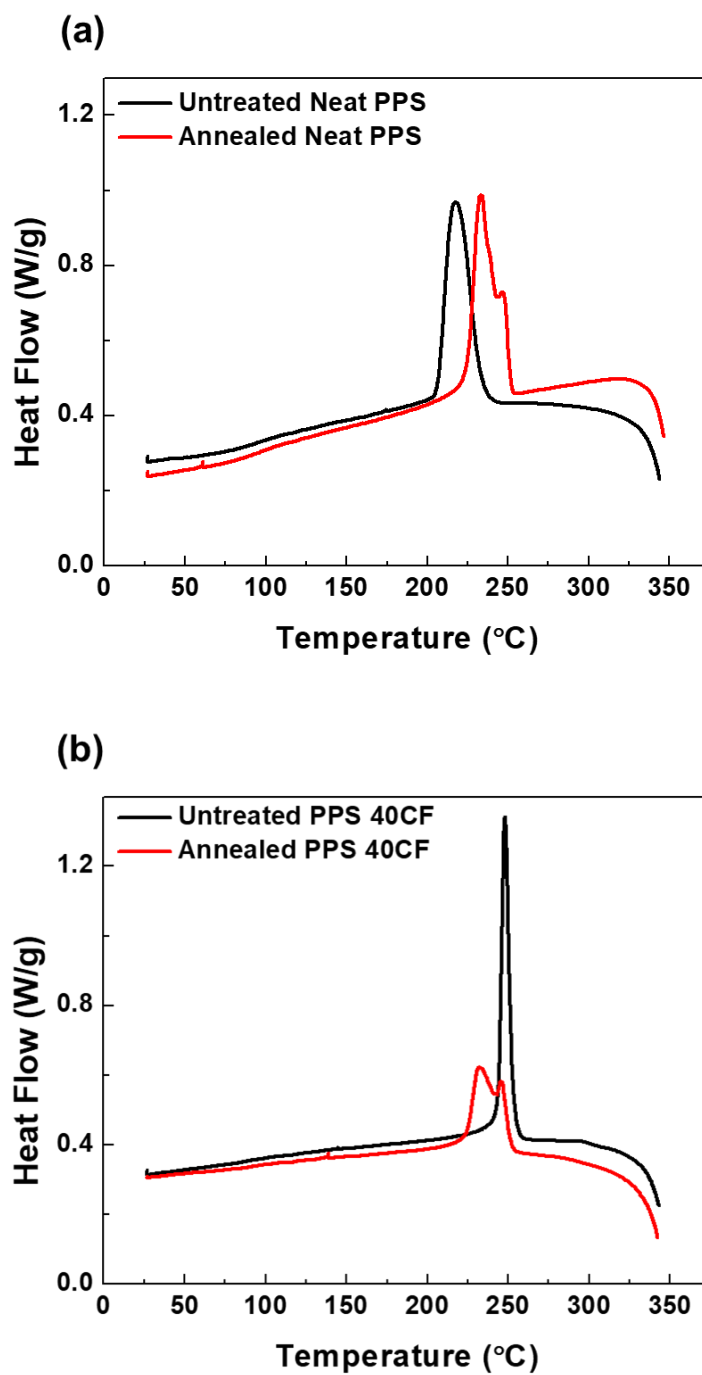
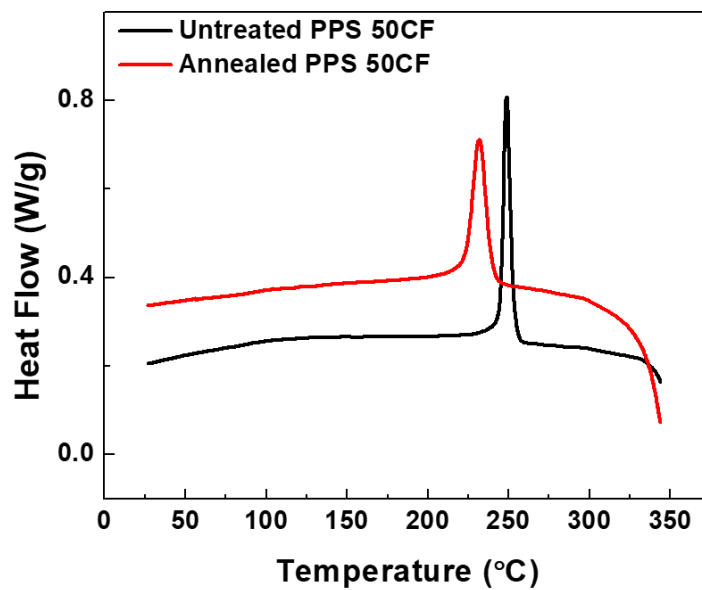


Figure 3.11 DSC analysis of cooling cycles for (a) Neat PPS, (b) PPS 40CF, (c) PPS 50CF and (d) PPS 60CF.

(c)



(d)

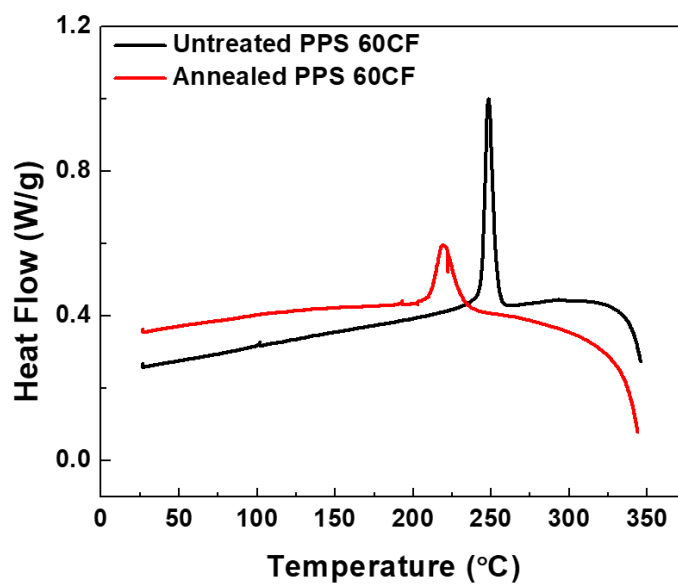


Figure 3.11 (continued).

Table 3.6 Analysis of DSC cooling curves.

Material	T_c (°C)		T_{onset} (°C)		ΔH_c (J/g)	
	Untreated	Annealed	Untreated	Annealed	Untreated	Annealed
Neat PPS	217.04	233.19	233.43	251.86	56.35	54.74
PPS 40CF	248.06	246.35, 232.44	252.79	251.45	35.75	26.6
PPS 50CF	248.87	232.11	253.21	239.51	20.17	18.65
PPS 60CF	248.44	219.04	253.83	222.72	22.65	14.81

3.3.3. Melt Rheology

To further elucidate the occurrence of oxidative reactions in the chosen grades of PPS due to annealing, melt rheological tests were also performed on both untreated as well as annealed pellets. The objective of these tests was to check for changes in viscosity which arise due to changes in the chemical structure of the polymer up on annealing. Since the samples are tested in their melt state at temperatures well above their T_m , all the crystallites would have been melted, thereby erasing the effect of crystallinity changes in the sample before testing. Any changes in the rheological properties would be due to structural changes taking place in the form of branching, chain extension and/or crosslinking, which can increase the molecular weight³⁴, and the viscosity of the melt (decreasing melt flow^{46, 81}). All tests were performed in the LVE regime of the material.

Figure 3.12 and Figure 3.13 represent the variation in complex viscosity with frequency for neat PPS and PPS 50CF samples (untreated and annealed) respectively.

Evidently, for both neat as well as the filled PPS, annealing led to an increase in complex viscosity at all frequencies by at least an order of magnitude. In addition, for neat PPS, the untreated sample showed a fairly Newtonian behavior. However, upon annealing the material exhibited shear thinning behavior. Such changes in viscosity indicate the occurrence of structural changes in the polymer (branching and/or crosslinking), for both neat as well as CF reinforced PPS due to annealing. To check if these reactions were oxidative, rheological analysis was performed on pellets annealed at 250 °C for 3 hr in air and in nitrogen separately on the DHR system. The viscosity of pellets treated in nitrogen for 3 hr was almost the same as that of untreated pellets, while the pellets annealed in air showed an increase in viscosity (Figure 3.14). This indicates that the structural change occurring due to annealing is oxidative in nature. Note that for all the rheological tests in this section, the tests were repeated at least twice for each condition with fresh samples to check for consistency, especially for the filled grades and the variation was within 20%.

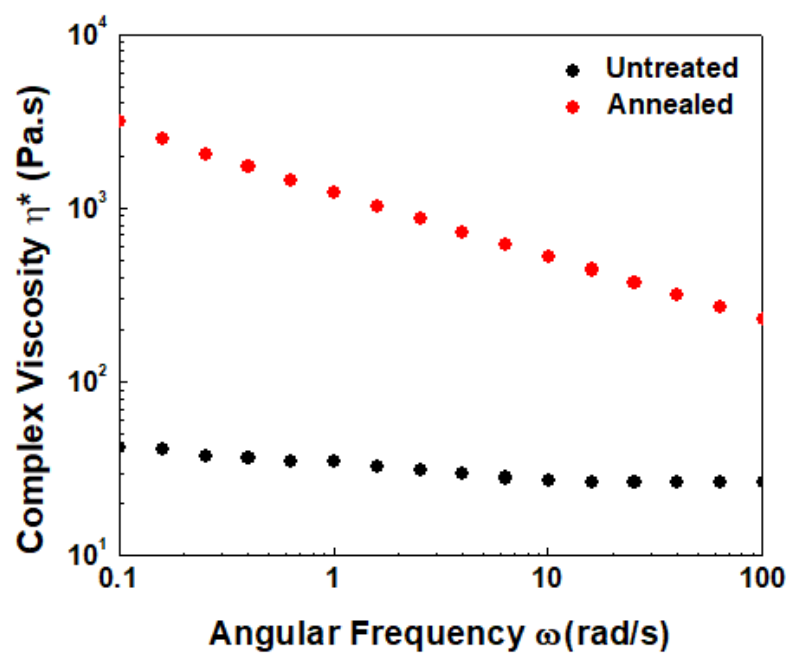


Figure 3.12 Effect of annealing on viscosity of neat PPS.

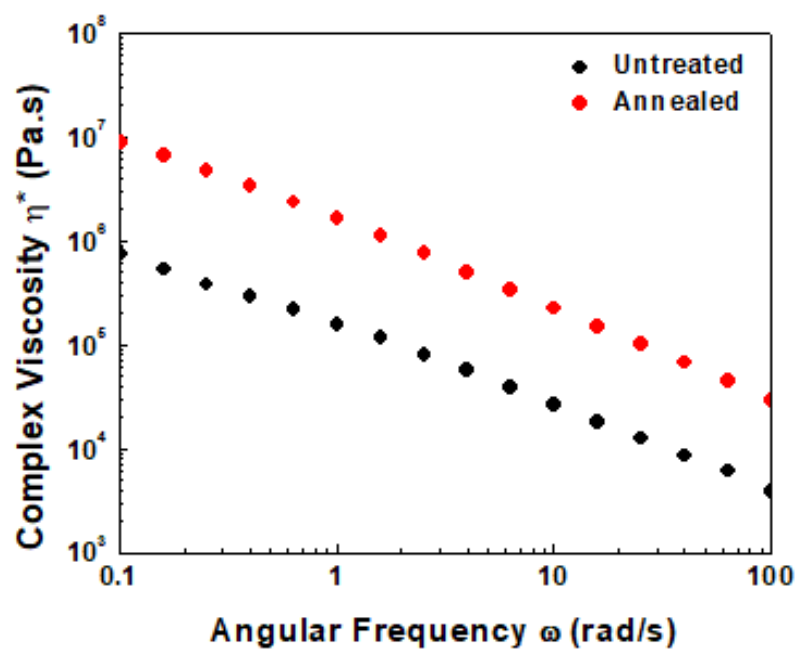


Figure 3.13 Effect of annealing on viscosity of PPS 50CF.

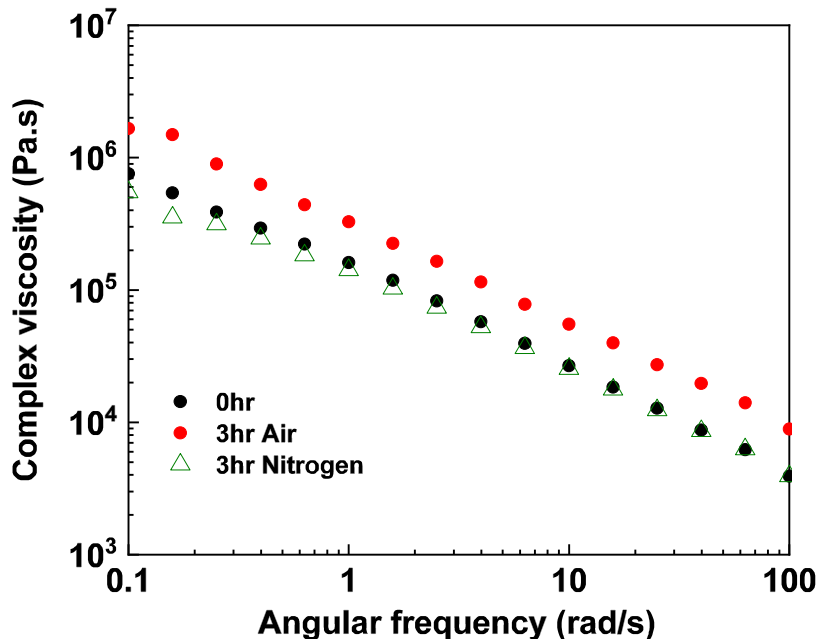


Figure 3.14 Effect of annealing environment on viscosity of PPS 50CF.

3.3.4. Fourier Transform Infrared Spectroscopy

FTIR analysis was performed on untreated and annealed PPS powder (powder was used for better contact with ATR probe) samples. From the obtained spectra as shown in Figure 3.15, both untreated and annealed samples showed peaks at 1572 cm^{-1} , 1469 cm^{-1} , 1385 cm^{-1} (stretching vibration absorption of the benzene ring skeleton in PPS), 1091 cm^{-1} (stretching vibration absorption of the C-S bond in PPS), and 807 cm^{-1} (characteristic peak of the p-disubstituted benzene ring), all of which corresponding to characteristic absorption peaks of pure PPS⁸⁵. Annealing in an oxidative environment (in air) introduced a new peak at 1044 cm^{-1} and also increased the intensity of the 1178 cm^{-1} peak. 1044 cm^{-1} peak can be attributed to aryl ether (C-O) linkage, indicating that the PPS has undergone oxidation up

on annealing⁸⁵⁻⁸⁶. The 1178 cm^{-1} corresponds to the stretching vibration absorption of $-\text{SO}_2$. This peak is present even in the untreated sample due to the low bond energy of C-S bond, which makes it easier for it to oxidize even during synthesis and drying process of PPS⁸⁵. However, up on annealing, the relative intensity of this peak increases, indicating an increase in the oxidation level. Therefore, FTIR data also supports oxidation taking place in PPS during annealing, which changes the chemical structure of the polymer.

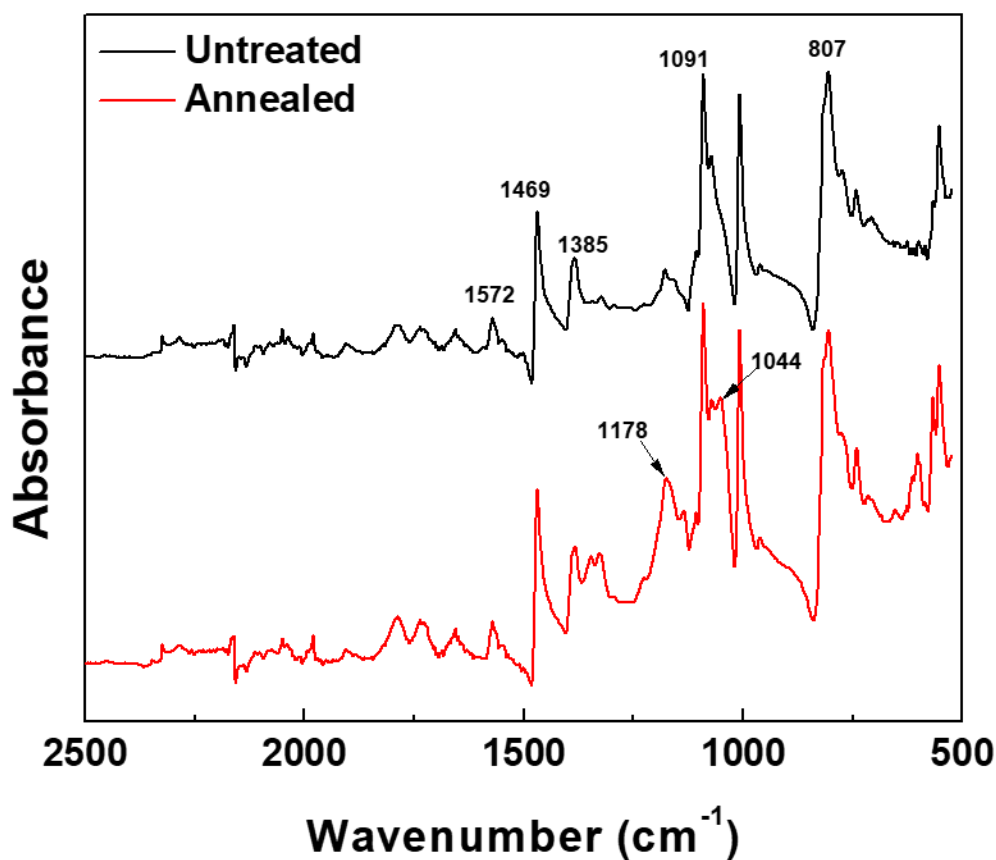


Figure 3.15 FTIR spectra for neat PPS.

3.3.5. Optical Microscopy

Effect of oxidation on surface vs bulk properties (Core/shell effect)

Analysis of DSC cooling curves, melt rheology and FTIR all indicate the occurrence of oxidative branching and/or crosslinking reactions in all four PPS grades up on annealing. Since these reactions have been identified to be oxidation driven, the influence of these structural changes on crystallinity can depend on the levels of diffusion of oxygen into the bulk sample. If this is the case, then the possible influence of crystallization and the mechanical properties by branching and/or crosslinking is limited by this step.

To investigate if oxidative reactions have occurred throughout the bulk of the samples tested for mechanical properties or only on the oxygen-rich surface, cross-sections of molded neat PPS were analyzed. Visual observation of the cross section of the sectioned annealed sample indicated the color change to be confined to certain depth close to the surface of the sample as shown in Figure 3.16. Optical microscopy revealed the thickness of the colored section (shell) to be about 500 μm on an average. The thickness of the colored section increased by about 150 μm when the annealing time was increased from 18 hr to 48 hr, indicating the color change to be due to oxidative reactions (not shown here). Since this indicated oxidation to be taking place in regions closer to the surface than the bulk of the sample, shell section (outer brown region) was separated from the core (inner white region) by sectioning on a diamond saw (Figure 3.17). The two separated regions were then tested for changes in crystallinity, possibility of structural changes and the effect of these on their mechanical properties separately.

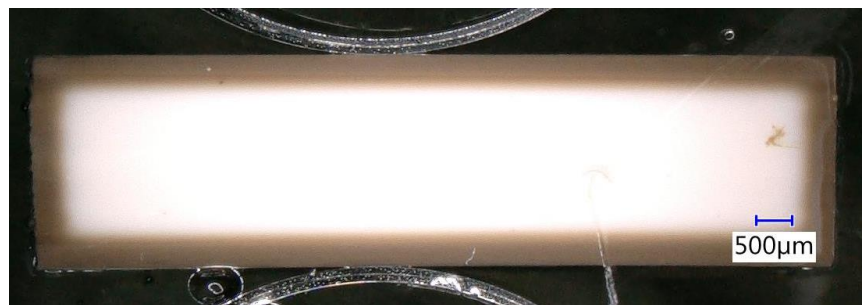


Figure 3.16 Optical micrograph of cross-section of annealed neat PPS sample.

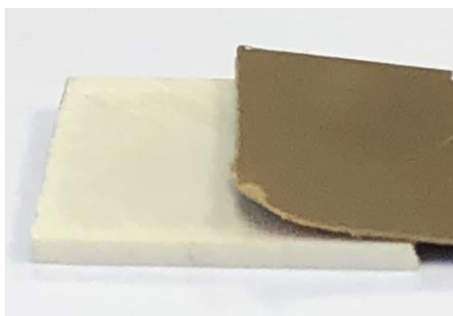


Figure 3.17 Separated core and shell sections of annealed neat PPS (sample dimensions: 25 mm X 25 mm).

3.3.6. Differential Scanning Calorimetry

Analysis of Core/Shell Sections

In the first heating endotherm (Figure 3.18a), the shell section exhibits double melting peaks, with a greater fraction of low melting crystals. The lower peak, as mentioned in the previous section, can be due to the formation of new crystal domains from the branches and/or crosslinks introduced due to annealing in this region which is closer to the oxygen rich surface. For the inner core section, this trend is reversed, i.e., the fraction of higher melting crystals is greater than the lower melting crystals, indicating reduced extent of structural change in PPS due to annealing leading to a reduction in the newly formed low melting crystals. However, the heat of fusion (indicated in Table 3.7) does not change for core and shell, indicating that the presence of branching and/or crosslinking does not influence degree of crystallinity as much. Analysis of the cooling cycle (Figure 3.18b) indicates shell to have a higher crystallization onset temperature and peak crystallization temperature (Table 3.7), indicating increased crystallizability due to the structural changes formed in this region with greater access to oxygen. Based on the analysis of core/shell sections, it can be understood that branching and/or crosslinking occurring due to annealing influences crystallizability more than the degree of crystallinity. This effect has been observed in some previous studies on PPS for samples possessing significant initial crystallinity ($\sim 65\%$)⁸¹ and annealing conditions below T_m .

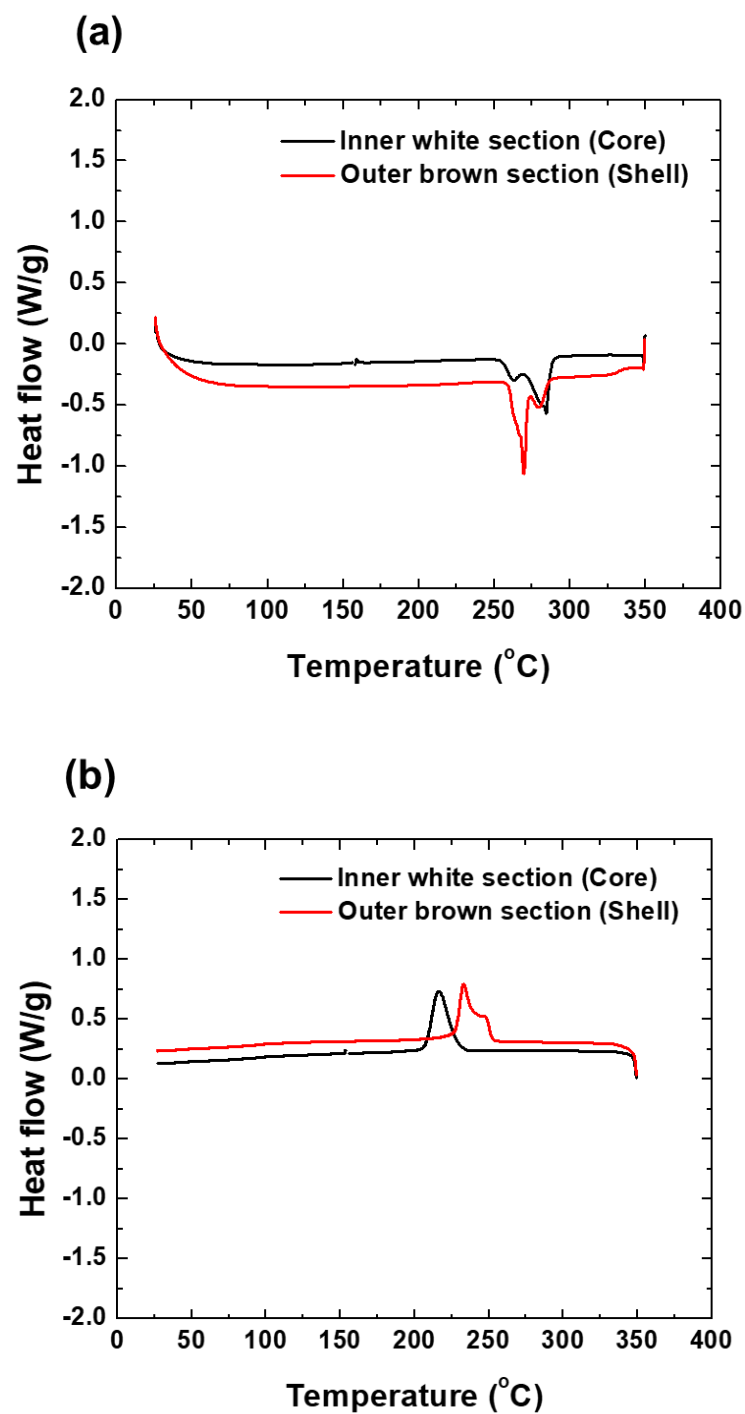


Figure 3.18 DSC thermograms for core/shell sections indicating (a) 1st heating cycle and (b) Cooling cycle.

Table 3.7 DSC analysis of core and shell sections separately.

Section	ΔH_f (1st heating cycle) (J/g)	T_{onset} (cooling cycle) (°C)	T_c (cooling cycle) (°C)
Shell	44.02	242.08*	233.23*
Core	43.10	228.52	216.45

*Based on second sharp peak.

3.3.7. Vickers Microhardness

Testing of Core/Shell Sections

To check for the effect of core/shell sections on the mechanical properties, Vickers microhardness tests were performed by indenting identified core and shell sections (as shown in Figure 3.19). The hardness of untreated sample was measured to be 24.13 ± 1.17 . Annealing led to an overall in hardness. However, there were no significant variations observed in the hardness values measured in the core regions (26 ± 0.56) and shell regions (27.25 ± 0.21), indicating that this property depends more on the degree of crystallinity and not necessarily the crystal size, which is altered by structural changes.

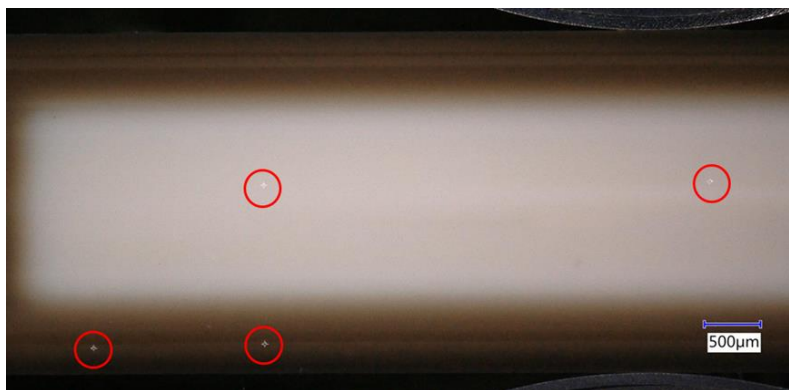


Figure 3.19 Optical micrograph indicating indentations from Vickers microhardness testing.

3.4. Summary and Conclusions

This work investigated the effect of annealing on mechanical properties of four different grades (neat and short carbon fiber reinforced) of polyphenylene sulfide (PPS). For all the four grades, annealing at 250 °C for 18 hr caused a small increase in the glass transition temperature (T_g), indicating an increase in the crystalline fraction. DMA analysis showed elastic modulus (G') to increase at temperatures above T_g , with the increase being greater at higher temperatures (Table 3.8). DSC analysis of as-annealed pellets indicated an overall increase in crystallinity for all the four grades, with the increase being the greatest for neat PPS. Further analysis cooling cycles indicated the crystallization temperature (onset and peak) to shift to higher temperatures for neat PPS but to lower temperatures for the three filled grades. This can be explained based on the possibility of branching and/or crosslinking happening up on annealing, which act as nucleation sites to enhance the rate of crystallization and crystallizability in neat PPS. However, in the case of filled grades wherein carbon fibers are already acting as nucleating sites, presence of

crosslinks impose constraints on chain mobility, thereby making it difficult for crystals to form.

Melt rheological analysis and FTIR analysis confirmed the occurrence of oxidation reactions which increase the melt viscosity and enhance shear thinning of neat PPS, indicating a structural change in the form of branching and/or crosslinking.

Visual observations of color change in the neat PPS up on annealing led to the cross-sectional analysis which indicated color change to be confined only to regions closer to the surface. DSC analysis of core (white inner section) and shell (brown outer section) indicated the shell section to possibly have more branches and/or crosslinks, thereby increasing the fraction of low melting crystal up on annealing. However, the overall degree of crystallinity did not change significantly between these two sections. Vickers microhardness tests performed on the core and the shell regions indicated hardness to be independent of the structural changes taking place due to annealing and more dependent on the overall degree of crystallinity.

Therefore, isothermal annealing of PPS parts improved mechanical properties by increasing the degree of crystallinity. Although annealing also led to oxidative reactions in PPS, the structural changes mainly influenced crystal size and crystallizability from melt and not necessarily the degree of crystallinity or the mechanical properties of PPS parts.

Table 3.8 Summary of the effect of annealing on mechanical properties of PPS parts.

Material/Print Orientation	ΔT_g (°C)	% Increase in G' at 50 °C	% Increase in G' at 175 °C	% Increase in G' at 250 °C
Neat/Molded	4.3	5	83	149
40CF/x-dir	4.1	-12	40	81
40CF/z-dir	4.2	2	42	124
50CF/x-dir	2.47	-3	14	63
60CF/x-dir	2.65	-6	16	115

Note that any variation less than 20% can be taken to be within the error limits and not significant.

4. Conclusions and Future Outlook

4.1. Summary of Research Work

The overall motivation for this work stemmed from the need to develop tooling for composites manufacturing (autoclave processing) using a process that is faster, cheaper, with short lead time and lower energy requirement when compared to traditional manufacturing processes, and by using materials that meet the mechanical and thermal properties requirements of a tool. The process selected was extrusion deposition additive manufacturing (EDAM) and the materials selected were carbon fiber reinforced grades of poly (ether ketone ketone) (PEKK) and polyphenylene sulfide (PPS).

4.1.1. Melt Processability of PEKK and PPS Composites

Research questions

The first section of this work focused on the following research questions:

- (i) What is the effect of key processing parameters on the melt flow characteristics of the chosen materials?
- (ii) Can rheological characterization be useful to identify suitable processing conditions to extrude the chosen materials on EDAM platform?

Overall conclusions

Primary conclusions from this work are:

- (i) Neat grades of PEKK exhibit greater thermal stability in air than the fiber reinforced grades and neat PPS also shows better thermal stability in air (at lower temperatures) than the fiber reinforced grades.

- (ii) Increase in temperature increases the viscosity build up for all the filled grades of PEKK and PPS with time, with the effect increasing with increasing filler loading. This indicates reduced thermal stability due to possible crosslinking reactions taking place at higher temperatures (with the presence of sizing on carbon fibers).
- (iii) Addition of carbon fibers increases the dynamic moduli, viscosity, as well as enhances the shear thinning behavior for both PEKK and PPS.
- (iv) The effect of temperature on viscosity is less pronounced for the filled grades of PEKK and PPS. Therefore, for BAAM processing, changing shear rate by varying the nozzle size or screw speed can be a better way to alter melt flow properties at the nozzle than changing the set temperature.
- (v) For BAAM processing of filled grades of PPS and PEKK, use of cover gas is recommended to minimize viscosity build-up.
- (vi) Overall, analysis of rheological properties of pellets prior to processing help in determining conditions suitable for EDAM processing.

4.1.2. Post-Processing Annealing of PPS Parts

Research questions

The second section of this work focused on the following research questions:

- (i) Does isothermal annealing have an effect on the mechanical properties of components printed using short carbon fiber reinforced PPS on large format EDAM platform?

- (ii) If there is an effect, which mechanism dominates, crosslinking or changes in crystallinity?

Overall conclusions

Primary conclusions from this work are:

- (i) Annealing does improve the mechanical properties (modulus) of 3D printed PPS components at temperatures above T_g .
- (ii) Changes in crystallinity is the dominating mechanism that determines changes in mechanical properties such as modulus (torsional) and hardness.
- (iii) Changes in polymer structure (oxidative reactions leading to branching and/or crosslinking) does occur due to annealing. However, its effect on mechanical properties at room temperature is not significant.
- (iv) Structural changes in the material due to annealing alters melt flow properties (only above T_m of the material).
- (v) Annealing leads to core/shell structure development (varying levels of oxidation) due to reactions driven by the presence of oxygen.
- (vi) Core/shell structure does not alter the degree of crystallinity but alters the size of crystal domains that form during annealing and reduce crystallizability from melt.
- (vii) The effect of core/shell structure on the mechanical properties (hardness) is not significant, indicating they are dependent more on the degree of crystallinity.

4.2.Future Outlook

This work, for the first time, reported a detailed melt rheological characterization of five different grades of PEKK and three different grades of PPS, both unreinforced as well as carbon fiber reinforced grades, across a wide range of shear rates, relating the effect of different EDAM process parameters on melt rheology. To better replicate the EDAM printing process, accounting for polymer chains and fiber orientation during flow and to be able to correlate data from small amplitude oscillatory shear (SAOS) tests with that from a capillary rheometer and the BAAM system, pre-shear process to preferentially align the fibers in the SAOS tests can be explored. The rheological characterization established in this work also sets a framework for understanding the viscoelastic properties of the chosen materials across a wide range of shear rates will be encountered in EDAM process. This can be helpful for the development of printability criteria that determines successful extrusion, stable bead formation etc. to be able to predict the printability of a material before processing on large scale systems.

The studies on post-processing isothermal annealing of PPS for the first time reported the effect of annealing on thermomechanical properties of large-scale parts printed using carbon fiber reinforced PPS. These studies revealed degree of crystallinity to be the major parameter influencing mechanical properties such as torsional modulus and hardness up on annealing. The studies also revealed the possible development of crystal domains of varying sizes across the thickness of the sample, depending up on the availability of oxygen for oxidative reactions occurring due to annealing. This indicates the possibility of crystal domains to be different even within a printed bead, depending up on the exposure to air,

thermal mass and the preferential redistribution of carbon fibers within a bead. Such studies could be very useful to shed light on the development of crystallinity within a printed bead and a part for EDAM processing and help tailor the final properties better.

4.3. List of Publications

Portions of this dissertation have been drawn from the following publications.

- (i) Kishore, V.; Chen, X.; Ajinjeru, C.; Hassen, A.A.; Lindahl, J.; Failla, J.; Kunc, V.; Duty, C., Additive manufacturing of high performance semi-crystalline thermoplastics and their composites. In *Proceedings of Solid Freeform Fabrication Symposium. Austin, TX* 2016.
- (ii) Kishore, V.; Ajinjeru, C.; Hassen, A.A.; Lindahl, J.; Liu, P.; Kunc, V.; Duty, C., Rheological characteristics of fiber reinforced poly (ether ketone ketone) (PEKK) for melt extrusion additive manufacturing. In *SAMPE Conference Proceedings. Seattle, WA* 2017.
- (iii) Kunc, V.; Kishore, V.; Chen, X.; Ajinjeru, C.; Duty, C.; Hassen, A. A., High performance poly (etherketoneketone) (PEKK) composite parts fabricated using Big Area Additive Manufacturing (BAAM) processes. *ORNL Technical Report ORNL/TM-2016/728* 2016.

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Vita

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