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THE EFFECT OF SHEAR-INDUCED FIBER ALIGNMENT ON VISCOSITY FOR 3D PRINTING OF REINFORCED POLYMERS

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Abstract

Material printed with large scale additive manufacturing systems such as the Big Area Additive Manufacturing (BAAM) system experience a wide range of shear rates during the extrusion process. The shear rate can vary over five orders of magnitude as the material passes through the single screw extruder and is deposited onto previous layers. When fiber reinforced materials are deposited, the fibers can become highly aligned in the direction of flow due to the high shear stresses experienced as the material passes through the nozzle. Therefore, accurate analysis of the viscoelastic response of a polymer during extrusion should replicate these conditions as closely as possible. This study evaluates the effect of a pre-conditioning shear strain on the extrusion viscosity of carbon fiber reinforced acrylonitrile butadiene styrene (ABS).

Introduction

Developing new materials and identifying existing materials that can be used for extrusion-based additive manufacturing (AM) processes, such as fused filament fabrication (FFF) and big area additive manufacturing (BAAM), of composites and thermoplastics is an area of interest in AM. An important characteristic to be taken into consideration in both new and existing materials is the behavior they exhibit during extrusion. This behavior is informed in part by the rheological properties of the material, especially the viscosity [1]. Rheological properties of various materials used in extrusion-based AM, ranging from commodity plastics such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) to high-temperature plastics such as polyphenylsulfone (PPSU) and poly (ether ketone ketone) (PEKK) have been studied [2-6]. The polymer melts used in FFF and BAAM display shear thinning behavior, where the viscosity decreases as shear rate increases [7]. Rheological properties of AM feedstock can be measured using either a parallel-plate rheometer or a capillary rheometer[8, 9]. On a parallel-plate rheometer, the sample is put between two plates and subjected to oscillatory shear at a specified frequency or frequency range, as shown in Figure 1's model, while controlling or measuring three factors: angular velocity, angular displacement or torque. These values are then used to find the rheological properties of the material such as the storage modulus, loss modulus, and complex viscosity [9]. A capillary rheometer on the other hand extrudes the molten plastic material through a die, and the force or pressure needed to extrude the material at a given rate is measured [9].An illustration of the capillary rheometer can be seen in Figure 2. The force or pressure and extrusion rate are then used to determine the rheological properties of the material such as the shear viscosity (reference) [9]. Parallel plate rheometers are best suited for low angular frequencies (0.01-628 rad/sec) and capillary rheometer are best suited for high shear rates (1000-10000 1/s) [9]. These two ranges can be correlated via the Cox-Merz rule for some polymers [10].

As the need for high-performance materials for AM with high specific modulus rises, so has the interest in carbon fiber reinforced polymers (CFRP) [11]. CFRP come in many different

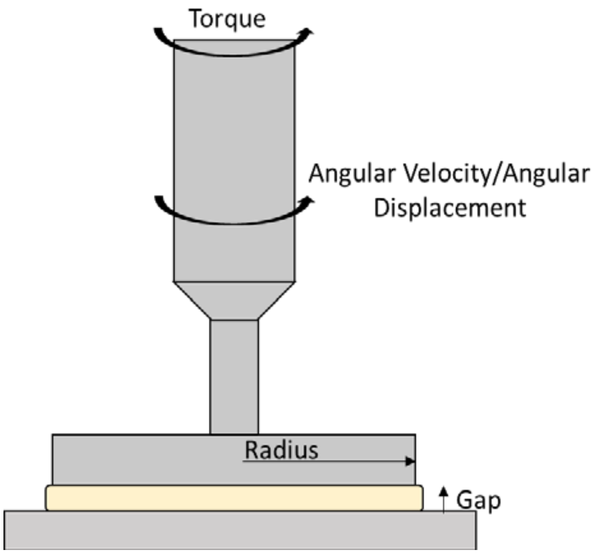

Figure 1. Model of parallel plate rheometer

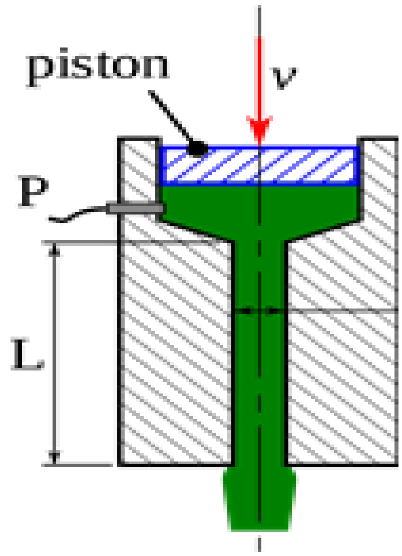

Figure 2. Model of capillary rheometer

shapes from manufacturers, such as sheets, filament or pellets. Pelletized feedstock is of interest to the authors as that is used in BAAM. Measuring the rheological properties of CFRP comes with different challenges depending on the type of rheometer used. In a parallel plate rheometer, it is suggested to use a gap of ten times larger than that of the longest dimension of the filler [12]. In pelletized feedstocks for BAAM, there can be fibers ranging from 50μm to 1000μm, this would require up to a gap of ten millimeters, which is far too large of a gap for a test to be conducted [4]. Pelletized AM feedstock tend to have some initial fiber alignment in the direction in which they were extruded [13]. When these randomly oriented fiber reinforced pellets, are loaded randomly onto the parallel-plate rheometer for testing, the CFRP will have random fiber orientation before and after they have been melted, as illustrated in Figure 3. When measuring complex viscosity data, the authors observed a large scatter in the data that is hypothesized to be a result of the random orientation of fibers in the sample during loading. Complex viscosity data of fiber reinforced thermoplastics from the parallel plate rheometer do not align with steady shear viscosity from the capillary rheometer data as it does for neat thermoplastics, which could also be due to differences in fiber alignment [14].

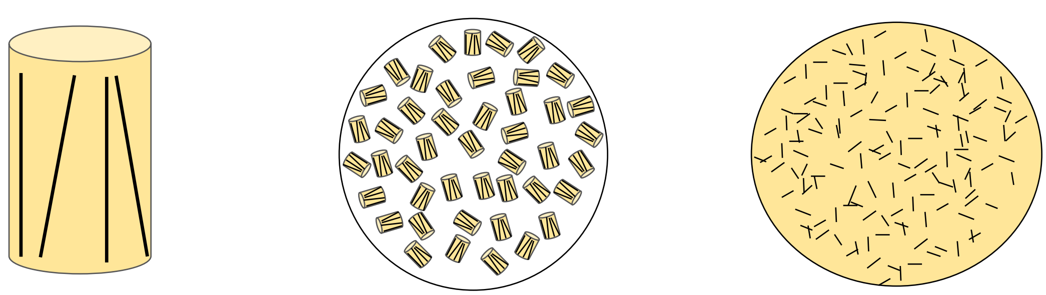

Figure 3. (from left to right) model of carbon fiber reinforced pellet, top-down view of a plate loaded with carbon fiber reinforced pellets, top-down view of melted random sample

In this work, the authors discuss the effects of applying a large shear strain to the sample before measuring the viscosity in parallel plate rheology, referred to here as “pre-shearing”. The goal of this work is to determine if and how pre-shearing influences complex viscosity data. Initial findings are reported using complex viscosity data of carbon fiber reinforced ABS recorded by the parallel plate rheometer on pre-sheared samples and compared with samples that have not been pre-sheared. The authors will also compare viscosity data from pre-sheared samples to capillary rheometer data for the same material.

Experimental

The material used for the experiments was ABS with 20% carbon fiber by weight in pelletized form. The tests were conducted on a Discovery Hybrid Rheometer 2 (DHR-2) from TA Instruments with 25 mm disposable aluminum plates. The DHR-2 uses the upper plate to apply shear to the sample and the lower plate is held stationary. The first step of the experimental process was to determine the linear viscoelastic region, the range of strains where the samples’ structure is not damaged by the experiment, of the carbon fiber reinforced ABS. The temperature selected for testing was 250°C, a common temperature for processing for 20%CF ABS, and the frequency chosen was 10 radians/second, an angular frequency similar to extrusion shear rates[15]. This established the strain and temperature that would be used for all the experiments: 0.1% and 250°C.

After the linear viscoelastic region was determined, the frequency sweeps were performed. For frequency sweeps, the aforementioned temperature and strain amplitude were used to collect complex viscosity data at a range of angular frequencies. Frequency sweeps were carried out on five samples from 0.1 rad/sec to 628 rad/sec. Each sample was loaded by depositing pelletized feedstock onto the plate with random orientation. The loading and melting of the sample can be seen in Figure 4.

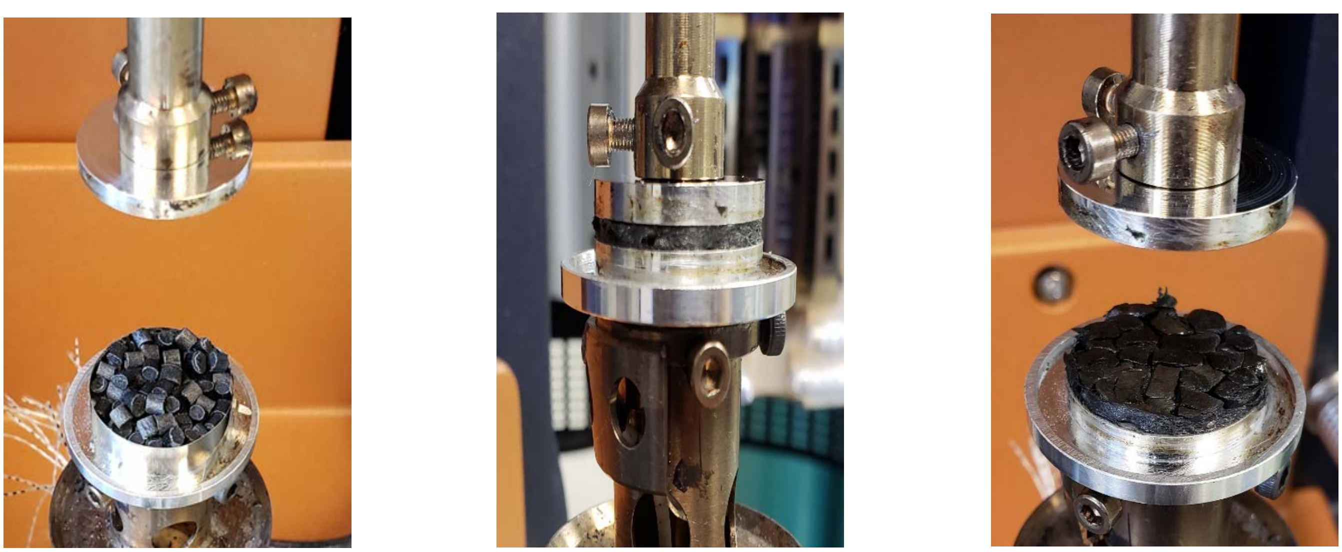

Figure 4. (from left to right) Pellets loaded in melt ring, pellets after melting, before testing, different view of pellets after melting, before testing

The next task was to determine a pre-shearing process that would be used as a comparison for the samples with no pre-shear. The pre-shearing process is defined as loading the pellets, melting them and lowering the upper plate to a chosen gap, and rotating the upper plate at a certain angular velocity for a set time prior to performing a typical frequency sweep on a sample. This process is depicted by the model in Figure 5. This process and variables were chosen after experimenting with numerous variations in displacements, velocities and other variables. The process is hypothesized to align the fibers with the direction of the shear they are subjected to, and this alignment of fibers would give data more relevant to extrusion, because fibers are aligned along the flow direction during extrusion [13]. Using the pre-shear process, the complex viscosity data of five samples was collected at 250°C and 0.1% strain. Viscosity data was also collected from a 3D printed spiral made from the same material, which would have high fiber alignment circumferentially, to compare the pre-shear process to a known high alignment sample.

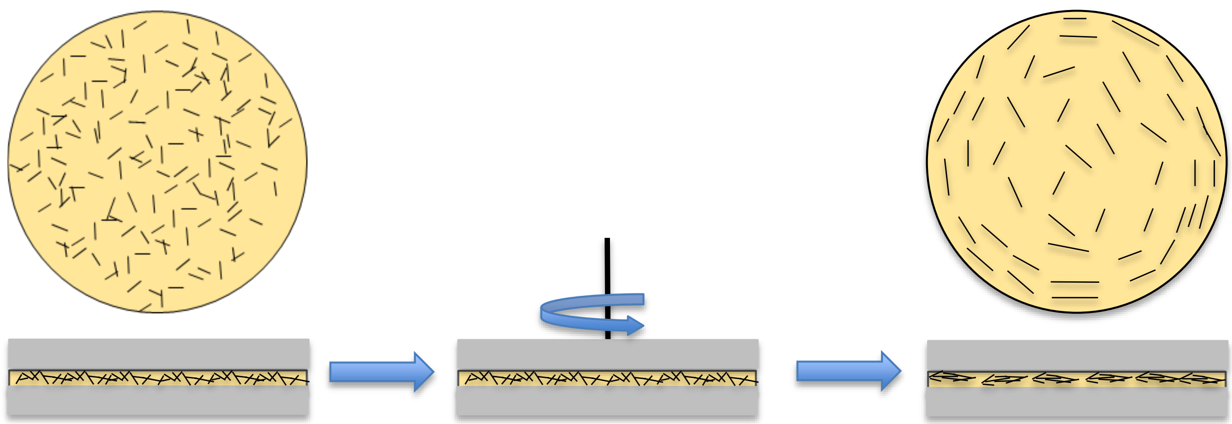

Figure 5. (from left to right) Model of both plates with melted random sample, model depicting the rotation of the upper plate to shear the sample, hypothesized model where fibers are given some alignment from the pre-shearing process

Data was also collected from the capillary rheometer and corrected for non-Newtonian flow using the Rabinowitsch correction and for excess pressure losses due to end effects using the Bagley correction [16, 17]. The Bagley correction was done by collecting data from 3 different die lengths and extrapolating what the viscosity data would be if the die length were zero, where there would be no pressure loss.

Results and Discussion

The data collected from the non-pre-sheared samples were all plotted together, shown in Figure 6. This graph shows the scatter that is often seen by the authors of this study when measuring complex viscosity of CFRP. This is an example of how getting repeatable and reliable data can be a challenge if there is no process to normalize or account for the scatter. Repeatable and reliable data will allow for more accurate comparison of data and possibly more meaningful insights about the data. The complex viscosity data from the five data sets are averaged, as shown in Figure 7, but even the averaged data is only representative of the viscosity data that would be collected from a sample with random fiber orientation. This data is less relevant to the extrusion process when the fibers are highly aligned. Therefore, moving forward, the task is to lower the scatter in the data and acquire data similar to extrusion from parallel plate rheology.

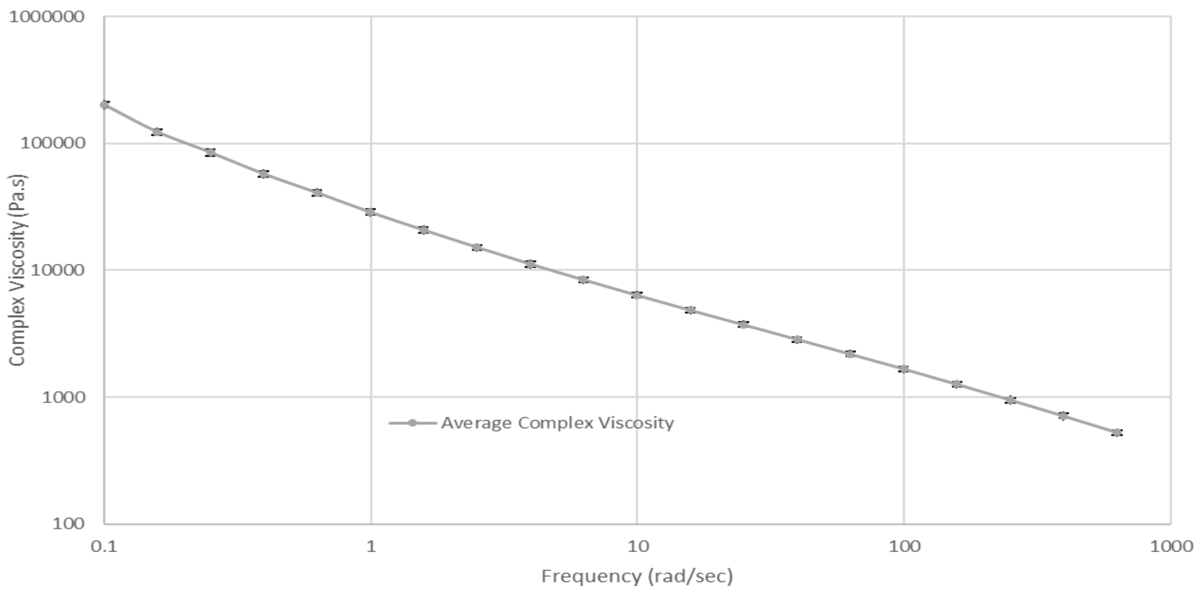

Figure 7. Average viscosity data from the viscosity data of 5 randomly loaded samples (20% CF ABS, 250°C, Air, 0.1% strain)

This may raise curiosity as to why capillary rheometer data is not used instead. This is because there is need for viscosity measurements at a wide range of shear rates and complex viscosity can still be used for determining appropriate processing conditions, such as a rise in temperature to lower the complex viscosity or complex viscosity increase from adding fibers to a polymer.

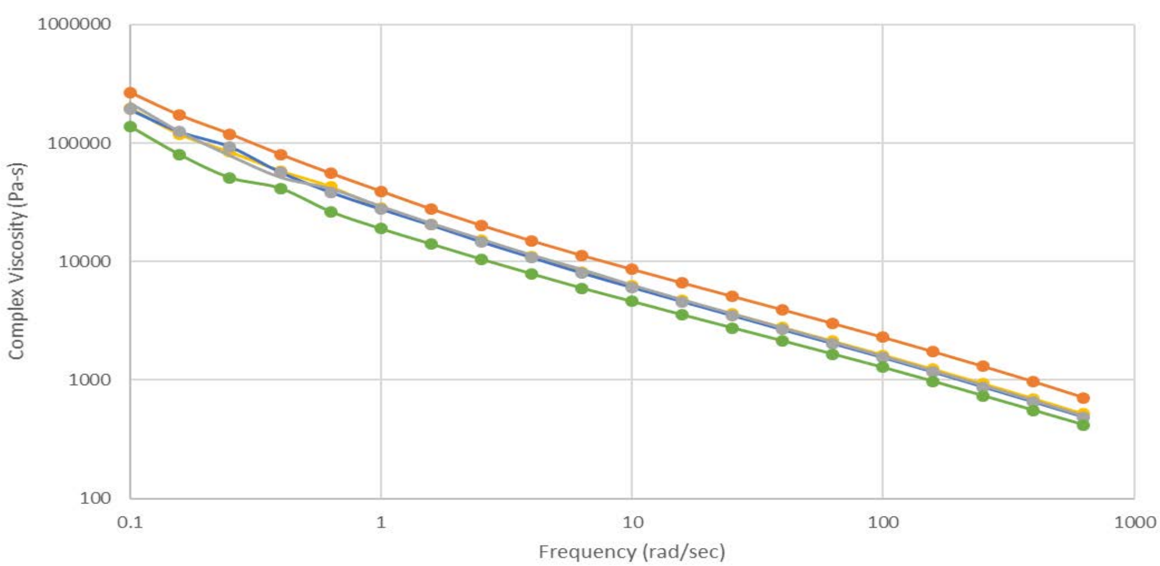

Figure 6. Scatter seen in viscosity data of randomly loaded samples (20% CF ABS, 250°C, Air, 0.1% strain)

The data from the five pre-sheared samples was also plotted to show the scatter of their recorded viscosity, this is displayed in Figure 8. The scatter of the normal samples with no pre-shear is also shown by the shaded area on the graph. The scatter in the data of the pre-sheared samples is lower by a minimum of 2.5 times and an average of 12.5 times, calculated via subtracting the lowest complex viscosity values (η*) from the highest complex viscosity values and comparing the values of the pre-sheared and non-pre-sheared samples, as seen in Equation 1. The process has provided more repeatable data for complex viscosity measurements of CFRP in parallel plate rheology. The pre-shearing process does have an influence on the scatter of viscosity data, a primary goal of this work.

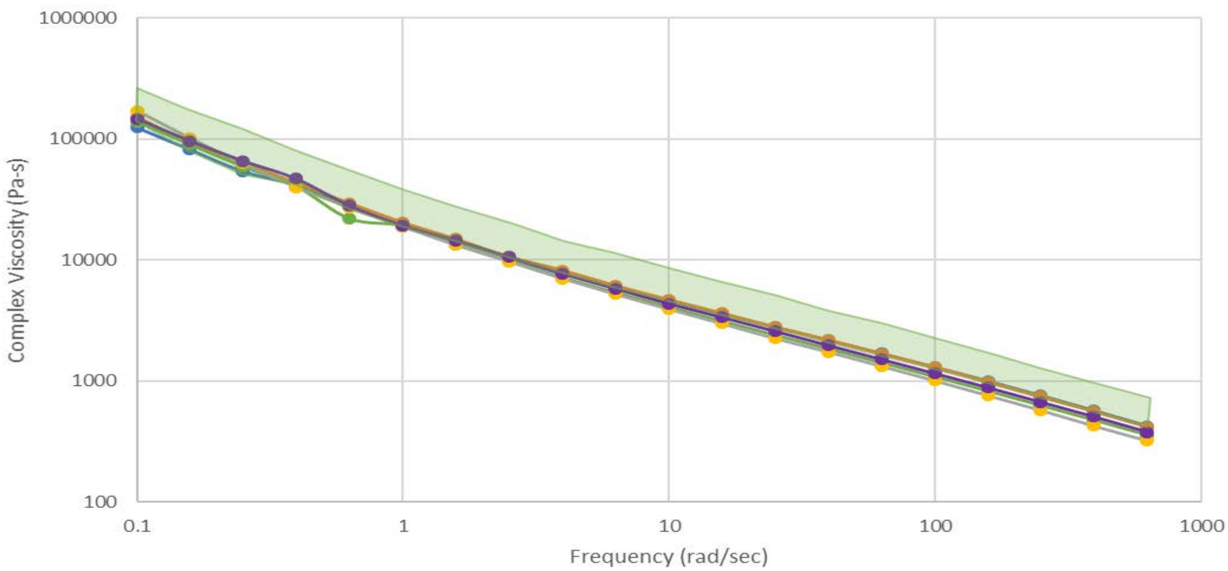

Figure 8. Graph of viscosity data of five presheared samples, overlayed with the range of viscosity of normal samples (20% CF ABS, 250°C, Air, 0.1% strain)

$$\frac{\eta_{upper,normal} - \eta_{lower,normal}}{\eta_{upper,pre-sheared} - \eta_{lower,presheared}} = Scatter\ Ratio \quad [1]$$

It may also be observed from Figure 8 that the range of pre-sheared complex viscosity data lies near the lower limit of the normal complex viscosity range. This led to a comparison of the averaged data from the two sample sets, which can be seen in Figure 9. The complex viscosity data of the pre-sheared samples was on average 30% lower than the non-pre-sheared sample, which is another way the pre-shear process affects the viscosity data from the 20% CF-ABS. This is thought to be due to shear alignment of the fibers in the sample, as hypothesized in the experimental section of this paper, since aligned fibers would lower viscosity and provide more process relevant data for extrusion [13]. This needs to be confirmed via microscopy or some other type of fiber orientation measuring process. This led to interest in how the pre-sheared data would compare to a sample with highly circumferentially aligned fibers, which is the direction of the shear from the rheometer. To compare the two, a 25mm spiral was printed from the same material, which, due to the extrusion aligning fibers in the flow direction, would have circumferentially aligned fibers [13]. This comparison can also be seen in Figure 9 along with an illustration of the printed spiral. The complex viscosity data of the printed sample aligned within 1% of the averaged data from the pre-sheared samples, giving more information suggesting that shear alignment of fibers may be taking place during pre-shear. This added information raised interest in how the pre-sheared viscosity would compare to capillary rheometer data for the same material, as the normal data had not aligned well with steady shear viscosity data from the capillary rheometer. The steady shear viscosity data from the capillary rheometer would have high fiber alignment as fibers align the direction of flow prior to extrusion [13]. These results are plotted together with the averaged complex viscosity data in Figure 9, and the steady state shear viscosity aligned more with the pre-sheared data than the normal data. The alignment of the pre-sheared complex viscosity results with the steady shear viscosity data from the capillary rheometer will be studied further in the future, but for now it acts as another indicator that the pre-shear process can be used to orient the fibers prior to small amplitude oscillatory measurements on a parallel-plate rheometer. Pre-shearing lowers viscosity and increases fiber alignment and these results correspond to what is observed from capillary rheometer data. The reason why the pre-shear process lowers viscosity must be further investigated in the future.

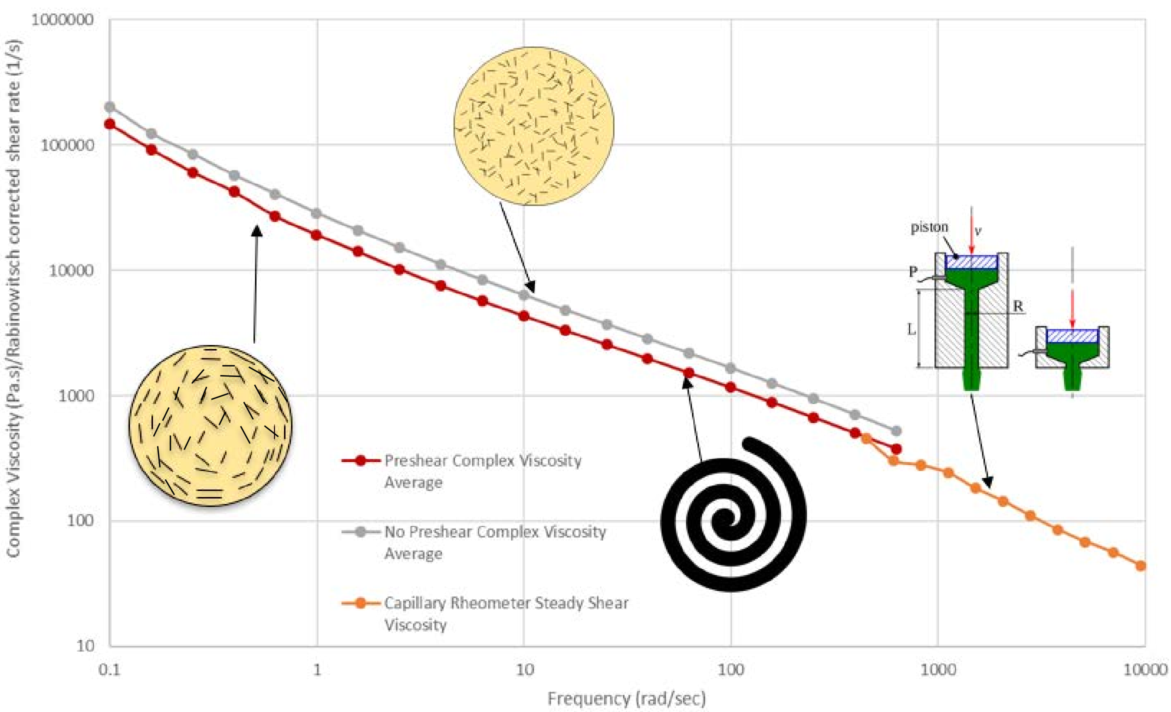

Figure 9. Graph comparing averaged viscosity data to viscosity data from a capillary rheometer and a printed specimen (20% CF ABS, 250°C, Air, 0.1% strain)

Conclusion and Future Work

This work discusses some issues that are encountered in parallel plate rheology when using CFRP and the authors approach to some of these issues, namely the pre-shearing process. The pre-shear process lowers the scatter in data when compared to normal samples by an average of 12.5 times, lowers viscosity by an average of 30%, and increases alignment with capillary rheometer data. The experimental results also show that the pre-shearing process may align the fibers, which will need to be studied more in the future via measuring fiber alignment in both the normal and the pre-sheared samples and comparing the values. There will also be more research into the alignment of capillary rheometer data and pre-sheared parallel plate rheometer data, as this could allow prediction of behavior at high shear rates without running capillary experiments, which is currently done with the Cox-Merz rule for neat polymers.

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