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The Influence of Rheology on Melt Processing Conditions of Amorphous Thermoplastics for Big Area Additive Manufacturing (BAAM)

Christine Ajinjeru[1,2], Vidya Kishore[1,2], Xun Chen[2], John Lindahl[2], Zeke Sudbury[1], Ahmed Arabi Hassen[2], Vlastimil Kunc[2,3], Brian Post[2], Lonnie Love[2], Chad Duty[1,2]

[1]University of Tennessee, Knoxville
[2]Manufacturing Demonstration Facility, Oak Ridge National Laboratory
[3]Purdue University

Abstract

This paper evaluates the influence of the rheological behavior of thermoplastics used in Big Area Additive Manufacturing (BAAM) on the melt processing conditions. An extensive rheological characterization has been conducted of two base resins; acrylonitrile butadiene styrene (ABS) and polyphenylsulfone (PPSU) as well as their composites containing reinforcing fibers. It was found that the unique processing conditions for each material is highly dependent on the rheological properties of these polymeric systems. A method is presented for considering rheological characteristics when selecting candidate materials suitable for the BAAM system and in developing processing bounds to achieve required material properties for applications such as high temperature tooling and composite structures.

Keywords: Rheology, Big Area Additive Manufacturing, Processing Conditions, Amorphous Thermoplastics

Introduction

Additive Manufacturing (AM), commonly referred to as 3D Printing, offers the ability to design and directly fabricate parts with complex geometry from a three-dimensional Computer-Aided Design (CAD) system. AM parts are made by adding material in layers wherein each layer is a cross-section of the part derived from the CAD file[1]. The most common AM technique is fused deposition modeling (FDM™), developed and trademarked by Stratasys in the 1990s. In FDM, a filament of an amorphous thermoplastic is fed into a heating element and it then becomes semi-molten. The melt is pushed through the print nozzle by the filament entering the heating element onto the print surface. Since the material is in a semi-molten state, the newly deposited layer fuses with the adjacent material that has been deposited. FDM uses a variety of unreinforced thermoplastics[1–3]. Those commonly used on the FDM system are available in filament form from several vendors and these include ABS, polycarbonate (PC), poly(lactic)acid (PLA), PPSU, polyetherimide (PEI) and blends such as PC/ABS and PEI/PC. Improvement in the mechanical properties of the parts made by AM has shifted the application of AM parts from prototyping to end-use applications.

Big Area Additive Manufacturing (BAAM) is a large-scale polymer extrusion based AM technique. BAAM is being developed at the Oak Ridge National Laboratory in collaboration with Cincinnati Inc. and is similar to FDM in that a molten thermoplastic is extruded along a tool path to generate a 3D part from a CAD file. However, instead of a heated chamber to melt the thermoplastic filament, BAAM uses a single screw extruder to melt pelletized feedstock[4]. Eliminating the need for a filament allows BAAM to leverage the cheaper industry standard feedstock such as pellets, powders, and reinforced thermoplastics. In addition, BAAM is able to make high-performance composite structures that contain significant amounts of fillers such as glass and carbon fiber reinforcements. Compared to the pure resin, fiber reinforced polymers increase the strength of the part by a factor of 4-7 times[5,6]. The single screw extruder in BAAM also increases the deposition speed up to 50 kg per hour. In addition, the build volume of the development can accommodate parts that are 6 m long, 2.4 m wide and 1.8 m high over a wide range of temperatures up to 510^{o}C[7]. Since BAAM enables large parts of complex structures to be fabricated cheaply and at reduced cycle times, the space for BAAM applications continues to grow. One of the potential applications for BAAM is in high-temperature tooling for target autoclave operations of about 175^{o}C, 6 bar. To achieve this, high-temperature and high-performance polymer systems need to be investigated as BAAM feedstock options.

This paper explores how the thermal and rheological behavior of two thermoplastics, ABS and PPSU, inform BAAM deposition temperatures and the screw speed. ABS is a commonly used and well characterized amorphous thermoplastic in FDM and BAAM processes. It is an engineering thermoplastic with a glass transition temperature of approximately 105^{o}C. PPSU on the other hand is a high performance amorphous, specialty engineering thermoplastic with high stiffness, good chemical resistance, flame resistance, and high glass transition temperature of 220^{o}C. The high glass transition temperature enables PPSU to be processed and utilized at high temperatures.

Since the BAAM system is capable of processing thermoplastics up to 510^{o}C, the challenge lies in identifying the range of temperatures at which thermoplastic materials can be successfully extruded at high temperatures without degrading and compromising structural integrity. Thus, rheology is used in this study to determine how the viscosity of the material changes at different processing temperatures and various filler loadings to provide a good predictor of what BAAM parameters (such as screw speed or temperature) can be changed to be able to attain a suitable viscosity for printing a functional part using BAAM.

Experimental

Materials

The ABS resin used was Lustran 433, obtained from Techmer ES and the 20 wt.% carbon fiber reinforced ABS used was a 3D printing grade, ELECTRAFIL J-1200 CF 20 NAT, produced by Techmer ES. The PPSU neat resin used was ULTRASON P 3010, produced by BASF. Two carbon fiber reinforced PPSU grades containing 25% and 35% by weight were used. The 25 wt.% and 35 wt.% carbon fiber reinforced PPSU used were a 3D printing grade, ELECTRAFIL PPSU 3010 CF 25 and CF 35 HS 3DP respectively, produced by Techmer ES.

Thermal properties

A differential scanning calorimeter (DSC Q2000) was used for thermal characterization to measure thermal transitions of the polymers. The weight of all samples was 9-10mg. The heating rate was 10°C/min and the materials were scanned from 25°C to 450°C. After the first scan, the samples were quenched at a rate of 5°C/min to 25°C and reheated as the second run. The ABS samples were scanned in air while PPSU samples were scanned under a nitrogen environment. A TGA Q500 thermal gravimetric analyzer was used to observe the degradation of samples. The heating rate for all samples was 10°C/min. ABS samples were heated to 600°C while PPSU samples were heated to 800°C. PPSU samples were equilibrated and held isothermal for 10 minutes at 348°C, 376°C and 393°C. ABS samples were degraded in air while PPSU samples were degraded in both air and nitrogen.

Rheological properties

Rheological properties of the ABS and PPSU resins and carbon fiber reinforced blends were measured using a Discovery Hybrid Rheometer-2 (DHR-2) on which parallel plates with a diameter of 25mm were mounted. The frequency range was set at 0.1- 628 rads^{-1} with an applied strain of 0.1% and 1% for ABS and PPSU, respectively. The applied strain utilized was selected was to be within the linear viscoelastic region of the specific polymer. The plate gap was between 1.5 and 2.5 mm. The ABS and PPSU samples used for rheology were in pellet form. The ABS and carbon fiber reinforced ABS samples were dried at 85°C for 4 hours before testing. The PPSU resin and carbon fiber reinforced PPSU pellets were dried at 120°C for 6 hours in a vacuum oven before testing. Measurements for ABS and carbon fiber reinforced ABS were made in air while those of PPSU resin and the carbon reinforced PPSU were made under nitrogen.

Results and Discussion

Thermal properties

The results of the differential scanning calorimetry (DSC) scans of ABS and PPSU are shown in Figure 1. ABS resin and ABS with 20 wt.% carbon fiber (CF) show the glass transition temperature (Tg) at 105°C. On the other hand, neat PPSU resin and CF reinforced PPSU show their Tg at 220°C. As expected, the addition of reinforcing fibers filler does not alter the base properties of the polymer matrix, and so the CF does not affect Tg. The glass transition temperature of PPSU is high, rendering PPSU suitable for high temperature use. Selecting the appropriate processing temperatures for these polymers on BAAM system is informed by Tg. In other polymer processing techniques such as polymer extrusion and injection molding, the temperature to extrude or mold thermoplastics is set at least 120°C above Tg. With this in mind, the lowest temperature for processing ABS and PPSU on the BAAM system based on DSC thermograms would be 225°C and 340°C respectively.

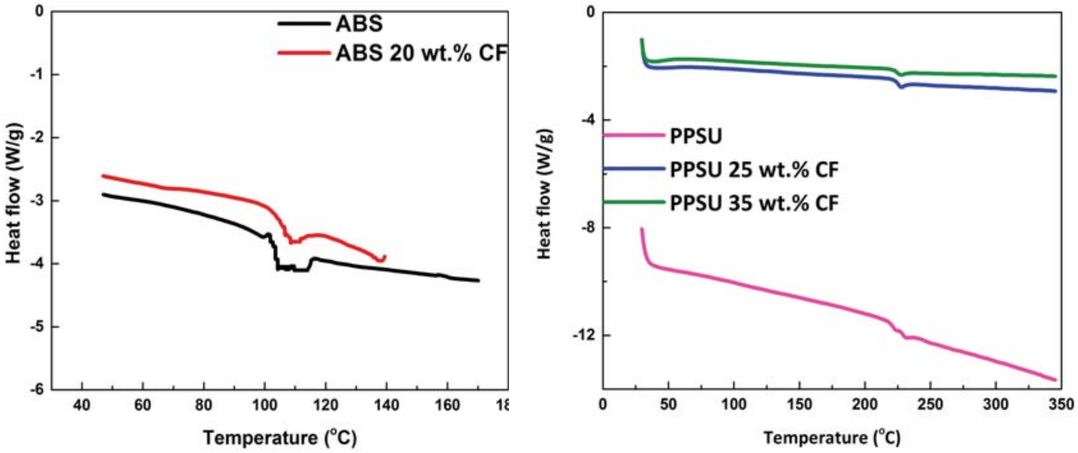

Figure 1. DSC thermograms of ABS and PPSU resins and CF reinforced blends.

Figure 2 shows the weight loss of ABS resin and CF reinforced blend measured by thermogravimetric analysis (TGA) in air. The decomposition onset temperature (DOT), described in this paper as the temperature at which 1% weight loss is observed for ABS and ABS 20 wt.% CF is 310°C. For printing purposes on the BAAM system, the upper limit on the processing temperature for ABS should not exceed 310°C because the matrix material starts to degrade and this could compromise the integrity of the BAAM part by reducing the stiffness. Reinforcing ABS with CF does not affect the DOT. The only difference is the residual weight loss at 370°C where 20% of the sample does not fully decompose in ABS 20 wt.% CF compared to ABS resin due to the 20 wt.% CF in the polymer composite.

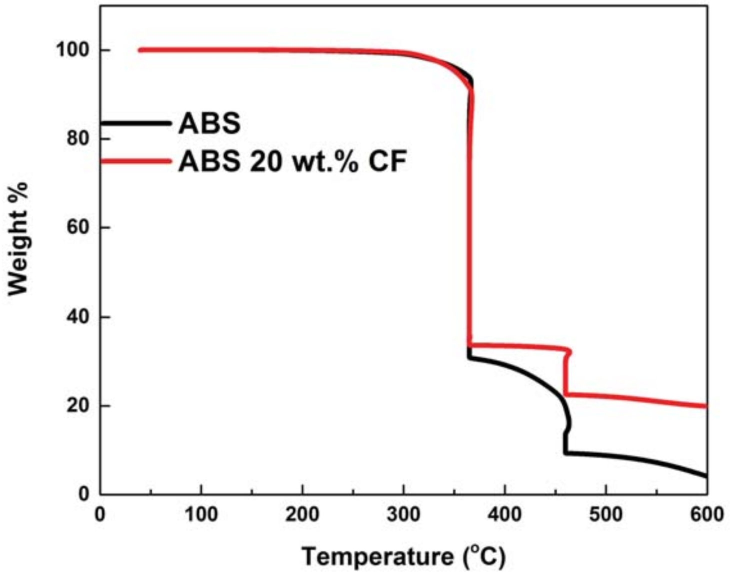

Figure 2. TGA thermograms of ABS (heating rate 10°C/min) in air

Figure 3 shows the weight loss of PPSU resin and CF reinforced blends measured by TGA in nitrogen. The DOT for PPSU and CF reinforced PPSU is 480°C in nitrogen. When measured in air, the DOT for PPSU resin decreases by 55°C to 425°C. As a result, if PPSU is to be printed on the BAAM system, an inert environment is required because PPSU decomposes faster when in air. Therefore, the upper limit for extruding PPSU, the upper temperature set point should not exceed 480°C under inert conditions. Similar to ABS TGA thermograms, reinforcing PPSU with CF does not affect the DOT.

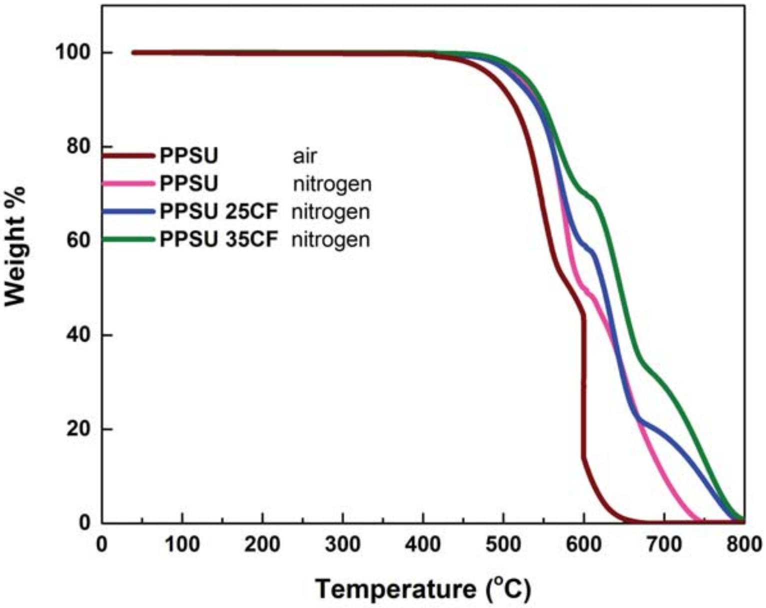

Figure 3. TGA thermograms of PPSU and CF reinforced PPSU blends (heating rate 10°C/min) in air and nitrogen

Determining Processing Temperatures for ABS and PPSU

Since the BAAM system is capable of processing thermoplastics at high temperatures of up to 510°C, the limiting factor in printing a thermoplastic material at high temperatures on BAAM is the temperature at which the material starts to degrade. TGA data for ABS and PPSU sets this temperature at 310°C and 480°C, respectively. The lower processing temperature is set 120°C above Tg as in polymer extrusion and injection molding industries. For ABS and PPSU, those temperatures are 225°C and 340°C respectively. These temperatures effectively set the upper and lower bounds for thermal processing.

Within these bounds, three candidate processing temperatures were selected for viscosity measurements for ABS (230°C, 250°C and 270°C) and PPSU (348°C, 376°C and 393°C). ABS and PPSU have been successfully extruded at each of these temperatures on the BAAM system, so this study focuses on characterizing the rheological behavior under relevant processing conditions.

Rheological Properties of ABS

Figure 4 shows the complex viscosity of ABS and CF reinforced ABS as a function of frequency at different temperatures. ABS is observed to be shear thinning at frequencies between 0.1 and 1000 rad/s for all processing temperatures. As the temperature is increased, the complex viscosity of ABS decreases by 50%. Addition of filler to the ABS resin, increases the viscosity of the composite relative to that of the neat resin by 65% and enhances the shear thinning effect of ABS. In BAAM, the shear rate at the nozzle is about 100-250s^{-1}, which is roughly equivalent to an angular frequency in this range. The viscosity of both neat and CF reinforced ABS is shear thinning in this region as viscosity decreases by 65%.

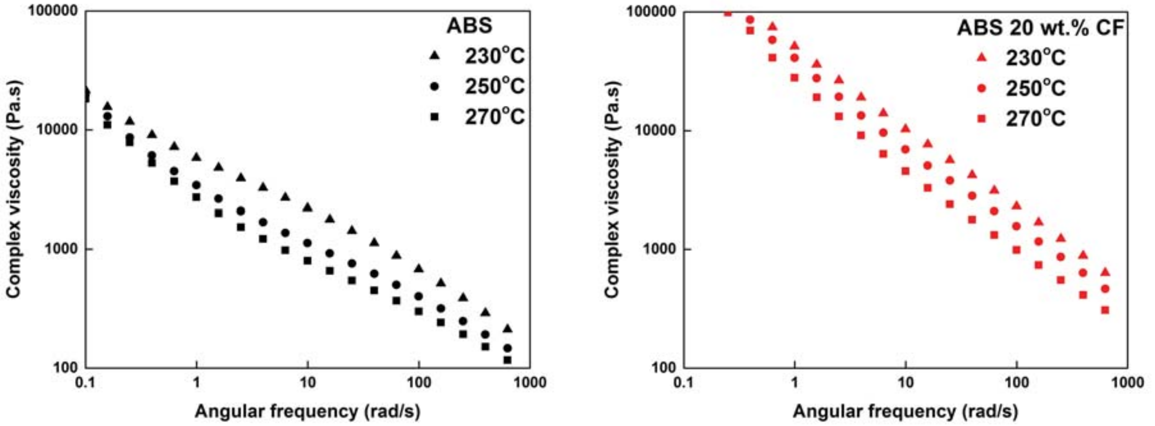

Figure 4. Complex viscosity versus frequency for neat ABS and ABS 20 wt.% CF at candidate temperatures

Rheological properties of PPSU

Figure 5 shows the temperature dependence of viscosity as a function of frequency at different temperatures and various carbon fiber loadings. In general, PPSU becomes more shear thinning at higher frequencies than at the lower frequencies. Increasing the temperature generally reduces the viscosity of the neat resin and that of the CF reinforced PPSU by 55%. On the other hand, addition and subsequent increase in CF loading in the PPSU resin, increases viscosity of reinforced PPSU by 300% compared to the neat PPSU resin at 348^{o}C.

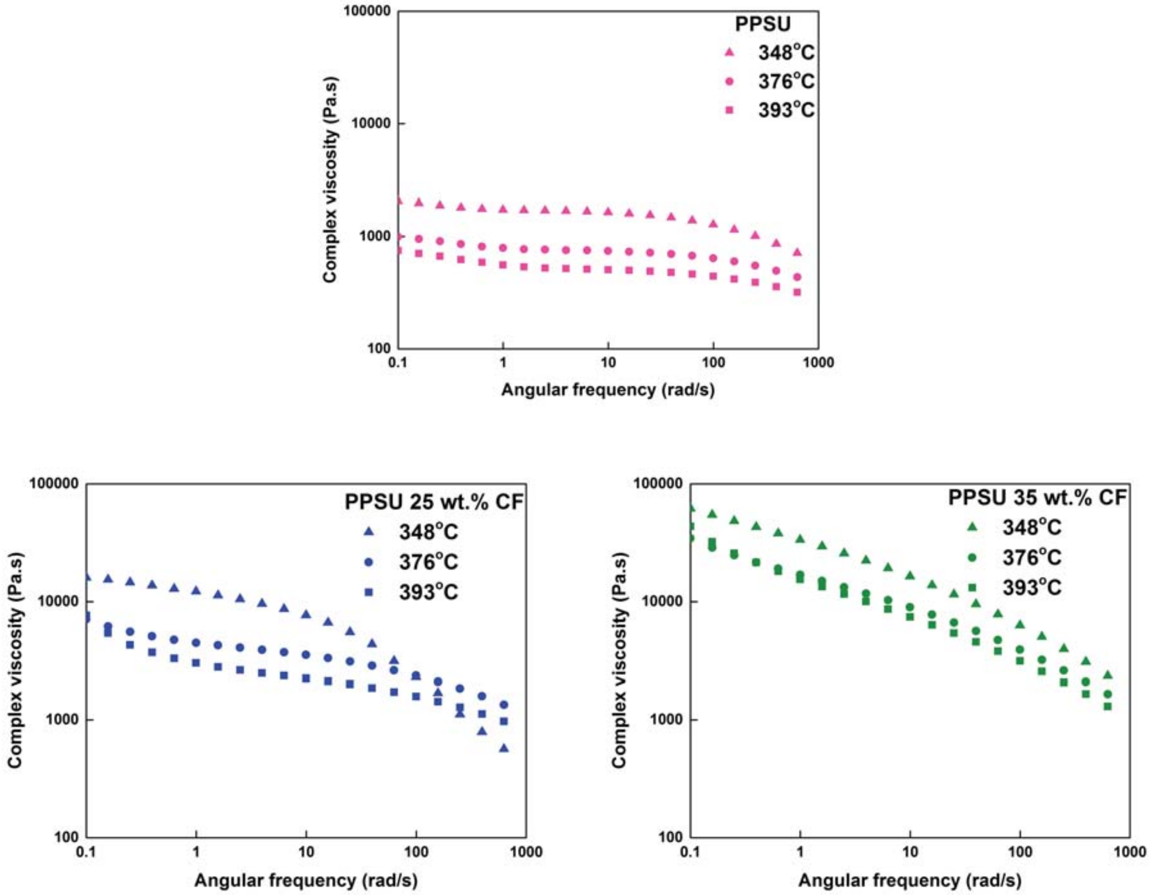

Figure 5. Complex viscosity versus frequency for PPSU and carbon fiber reinforced PPSU at candidate temperatures

In the 100-250s^{-1} shear rate range of interest for BAAM, an increase in the processing temperature reduces the viscosity of PPSU by 55% and enhances the shear thinning effect. Viscosity in this region (100-250s^{-1}) decreases by 65% with increasing shear rate for both neat and reinforced PPSU. This means that when processing CF reinforced PPSU on the BAAM system, both temperature and shear rate are effective parameters for controlling the viscosity of the extruded material, as long as the temperature chosen is below the decomposition temperature.

Conclusion

For thermoplastics to be processed and printed on the BAAM system, they need to be stable over a range of processing temperatures in order for the end part to possess the desired strength and modulus associated with these thermoplastics. The use of thermal characterization techniques; TGA and DSC to identify the glass transition and onset of decomposition temperatures respectively, allows for an educated judgement to be made when choosing deposition temperatures by setting the upper and lower bounds on appropriate processing temperatures. The rheological behavior of thermoplastics at various temperatures and shear rates helps to identify the process parameters that can effectively control the ability to successfully extrude and print on BAAM. The rheology of the two thermoplastics studied in this paper: ABS and PPSU, was found to vary as a function of frequency at different temperatures, shear rates and various carbon fiber loadings. The viscosity of ABS and PPSU decreased by 50-55% with an increase in temperature. The addition of CF to the neat resins increased the viscosity of ABS by 65% and that of PPSU by 300%. The 300% increase in viscosity for PPSU is attributed to higher filler loadings of 35 wt.% compared to only 20 wt.% for ABS. As the shear rate increases from 100-250s^{-1}, viscosity of ABS and PPSU both decreased by 65%. The strong impact of various process parameters on the viscosity of high performance thermoplastics indicates the value of understanding the rheological behavior of candidate materials for printing with BAAM and similar thermal extrusion systems.

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