Rheological evaluation of high temperature polymers to identify successful extrusion parameters

Christine Ajinjeru[1,2], Vidya Kishore[1,2], Peng Liu[2], Ahmed Arabi Hassen[2], John Lindahl[2], Vlastimil Kunc[1,2,3,] Chad Duty[1,2]

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

Abstract

With the advancements in additive manufacturing (AM), several high temperature thermoplastics are being explored as potential AM feedstocks. Some of these high-performance thermoplastics include; polyetherimides (PEI), polyphenylsulfones (PPSU/F), poly (ether ketone ketone)s (PEKK) and polyphenylene sulfide (PPS) as well as their reinforced composites. Most of these advanced resins tend to be more expensive than commodity plastics such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA), and their processing parameters have not been determined for most AM systems. This paper demonstrates a method for identifying the appropriate processing conditions for extrusion-based AM deposition systems, in which a material is forced through an orifice at a given flow rate. The pressure required to extrude a shear-thinning thermoplastic at a given shear rate is calculated based on viscoelastic properties of the polymer melt and compared against maximum system pressure to predict successful extrusion. An evaluation of several candidate materials is presented on the Big Area Additive Manufacturing extrusion-based platform.

Introduction

Additive Manufacturing (AM), commonly referred to as 3D printing, offers the ability to design parts with complex shape and geometry directly from a Computer Aided Design (CAD) file [1]. AM techniques have been developed over the years and can process a variety of materials such as wood, ceramic, metals, and polymers [2]. There are various forms of 3D printing systems that rely on the extrusion of polymer materials such as Fused Filament Fabrication (FFF), Big Area Additive Manufacturing (BAAM), and Direct Write (DW). The BAAM system under development at Oak Ridge National Laboratory is a large-scale polymer extrusion based AM technique capable of depositing thermoplastics at temperatures of up to 500 °C. BAAM uses a single screw extruder to melt pelletized feedstock and is capable of building parts that are 6 m x 2.4 m x 1.8 m, which are about 10 times bigger than commercial AM systems. BAAM can process a wide variety of thermoplastics including reinforced materials which provides additional strength and stiffness [3–5].

Historically, AM has proven useful for making models and prototypes. However, the number of applications is increasing as the processes develop and improve to utilize specialized and high-performance thermoplastics. Due to the high cost of the base resins of the high-performance thermoplastics, a screening methodology is necessary to prevent costly trial-and-error on AM systems especially BAAM that deposit at rates that exceed 50 kg per hour. Discrete modeling efforts have been pursued for the pressure drop in an FFF process [6], the conditions for a successful bond between adjacent deposited beads [7], and the thermal history of both FFF and BAAM systems [8]. However, a unified model has not previously been proposed for the successful extrusion of polymers for 3D printing.

The authors of this study have recently introduced a practical model for evaluating the printability of polymer feedstock materials for extrusion-based 3D printing platforms, described in detail in [9,10]. The proposed model introduces a four-part framework to assess the printability of thermoplastics on extrusion-based AM systems using a simple viscoelastic model. For successful printing at a basic level, pressure-driven extrusion must first occur through a nozzle of a given diameter at a given flow rate. Second, the extruded thermoplastic material must form a stable bead of the desired shape. Third, the extruded bead must exhibit basic functionality, such as bridging a free spanning gap and supporting subsequent layers. Finally, the 3D printed structure must be dimensionally stable during the transition to the final state – either via cooling to ambient temperature or chemical curing. The current study focuses on the first printability criteria; pressure-driven extrusion through a nozzle of given diameter at a specific flow rate on BAAM. This criterion is evaluated using example test cases: ABS, a commodity thermoplastic commonly used on BAAM, and two high performance thermoplastics, polyphenylsulfone (PPSU) and poly (ether ketone ketone) (PEKK) as well as their carbon fiber reinforced composites.

ABS and PPSU are amorphous thermoplastics with glass transition temperatures of approximately 105 °C and 220 °C, respectively. Few studies have been published related to the use of ABS and PPSU as well as their fiber reinforced composites on BAAM [11,12] or their rheological behavior with regard to AM [13,14]. PEKK is a high performance semi-crystalline polymer belonging to the poly (aryl ether ketone) (PAEK) family. Thermal analysis of various grades of PEKK have determined appropriate temperature ranges for characterizing the polymer melt [15]. In addition, rheological properties of these PEKK grades have been evaluated to determine the impact of temperature, time, processing environment, reinforcing material, and shear rate for extrusion based AM application [16].

Approach

Deposition System Parameters

The extrusion-based system of interest for this study is BAAM. The common printing parameters as well as their definitions for each of the BAAM system are described below. An illustration of the basic extrusion geometry is shown in Figure 1 with the independent variables for each extrusion-based process listed in Table 1.

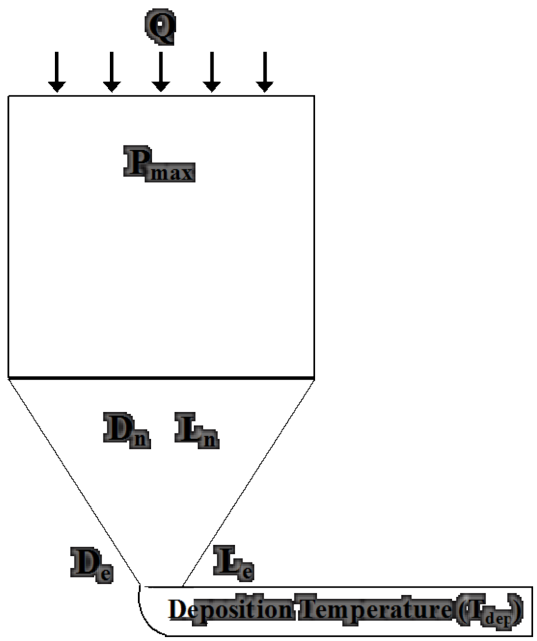

Figure 1. Deposition parameters for typical extrusion-based deposition platforms.

Table 1. Typical printing parameters for BAAM.

Parameter	**BAAM**	**Units**
Volumetric Flow Rate of extruded material (Q)	5.25	cm^3/s
Maximum system pressure (P_{max})	6.89	MPa
Diameter at the exit of the extrusion head (D_E)	0.76	cm
Length of the extruder exit region (L_E)	0.86	cm
Diameter of the nozzle leading up to the extruder exit (D_n)	1.02	cm
Length of the nozzle leading up to the extruder exit (L_n)	6.4	cm

Modeling Pressure-Driven Extrusion

The first step in the extrusion-based deposition process (identified as Mode Ia in [9,10]) is the ability for the molten thermoplastic to be forced through a nozzle of given diameter at a given flow rate at a pressure that is below the system limit. For simple viscous flow, this is dependent on the viscosity of the material at the operating shear rate. A material is considered to meet this condition if it can achieve the required volumetric flow rate under the typical system pressure. This criterion does not take into the account the role of reinforcing fibers during extrusion, aside from their effect on apparent viscosity. A secondary condition is used in the printability model [9] when using fiber reinforced materials – namely Mode Ib in which the fibers have the potential to entangle as they approach the flow restriction of the extrusion orifice and clog the nozzle.

At a basic level, the extrusion of common thermoplastics used in BAAM can be modeled as simple viscous flow through a circular nozzle. To model the flow of the polymer melt through the nozzle, pressure-driven flow (Poiseulle flow) assumes no slip occurs between the wall and the melt, and the velocity is highest at the center and zero closest to the wall. The pressure required to extrude a shear-thinning fluid at a given shear rate ($\dot{\gamma}$) through a nozzle of radius (R) and length (L) is thus calculated by:

$$\Delta p = \frac{8\,\eta\,Q\,L}{\pi\,R^4} \quad [1]$$

where Q is the volumetric flow rate and η is the viscosity of the polymer melt at deposition temperature. For extrusion on a typical BAAM nozzle using this proposed model, the total pressure drop is a summation of the pressure drop along the nozzle and through the smaller diameter exit. The length and diameter of the nozzle are denoted by L_n and D_n respectively while the length and diameter at the exit of the nozzle are identified as L_E and D_E respectively (Figure 1 and Table 1).

Polymeric materials used for 3D printing are typically non-Newtonian, shear-thinning, at the deposition temperature (T_{dep}). For a shear-thinning fluid, the viscosity (η) is related to the shear rate ($\dot{\gamma}$) through a power law relation:

$$\eta = C\,\dot{\gamma}^{(n-1)} \quad [2]$$

where C is a constant and *n* is the power law index. The smaller the *n* value, the more shear thinning the polymer is. The shear rate ($\dot{\gamma}$) is determined by the volumetric flow rate (Q). A Rabinowitsch correction [17] (Eq.3) is made for the shear rates of shear thinning polymer melts to account for the non-parabolic flow at the wall:

$$\dot{\gamma} = \frac{4Q}{\pi R^3}\left(\frac{3n+1}{4}\right) \quad [3]$$

<u>*Print criteria:*</u> if a material is to be successfully extruded on BAAM, the calculated pressure drop (Δp) needed to achieve the desired volumetric flow rate (Q) must be less than the maximum system pressure (P_{max}). On the current BAAM system, P_{max} is set at 6.89 MPa. Failure to meet this criterion does not mean that the system will clog, but that the material will not be extruded at the desired volumetric flow rate (Q). The rheological property needed to evaluate a material under this condition is the viscosity (η) as a function of shear rate ($\dot{\gamma}$) at the deposition temperature (T_{dep}).

Results and discussion

Evaluation of sample materials for pressure-driven extrusion flow

The viscoelastic properties of three materials; ABS, PPSU and PEKK as well as their fiber reinforced composites are used to evaluate the practical application of the model on the BAAM system (Table 2). Previous rheological characterization investigation studies on these polymer systems were performed on a Discovery Hybrid Rheometer-2 (DHR-2) parallel plate rheometer identified the linear viscoelastic (LVE) region from strain sweep measurements at select temperatures. Frequency sweep tests were then carried out in the LVE region to monitor and quantify the effect of the processing temperature, carbon fiber loading and shear rate on the complex viscosity and dynamic moduli of these polymer systems [14–16,18]. Note that only C and n from equation 2 are used to describe viscosity of the material over the linear region approximating the extrusion shear rates.

Table 2. Materials and print conditions for pressure-driven flow criteria

	ABS		20% CF ABS		PPSU		35% CF PPSU		PEKK		40% CF PEKK	
Tg (°C)	105		105		220		220		158		158	
Tm (°C)	-		-		-		-		316		316	
*DOT (°C)	380		380		480		480		> 500		> 500	
Tdep (°C)	230	270	230	270	348	393	348	393	375	390	375	390
n	0.5	0.41	0.29	0.24	0.94	0.92	0.67	0.62	0.84	0.83	0.58	0.51
C (Pa s^n)	6974	3152	52905	40285	1987	606	35067	17875	1393	1365	29724	29372

*DOT – decomposition onset temperature; temperature at which 1% weight loss is observed in a thermal gravimetric analysis thermogram

The variations among these materials demonstrate the effectiveness of the proposed model in predicting successful extrusion conditions. For thermoplastics to be successfully extruded and subsequently printed on any extrusion-based AM system, they must be in the molten state. The viscosity of these materials was measured at two temperatures; a low temperature determined by the lower processing limit of each material and a high temperature that was below the decomposition temperature of the material. The temperature at which each material is processed is dependent on its glass transition temperature (T_g), melt temperature (T_m) for semi-crystalline materials and the decomposition temperature [14,15] (Table 2). Since interlayer bonding is thermally driven, there is an advantage to processing the polymer melt at higher temperatures.

High performance thermoplastics such as PPSU and PEKK can present a unique challenge when it comes to determining the appropriate deposition temperatures on BAAM. These materials should be heated high enough so that it flows but not so high that it thermally degrades or crosslinks. Previous studies on PPSU and PEKK composites utilized thermal characterization techniques, namely differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), to set the lower and upper processing temperatures respectively of these polymer systems for extrusion-based AM systems. The temperatures used in this rheological model lie within the deposition temperatures recommended for these polymer systems [14,15].

Varying the temperature of polymers changes the viscosity which in turn affects the volumetric throughput capability for extrusion through the nozzle (Figure 2). Over the shear rates of interest (~30 – 40 s^{-1} in the nozzle and ~100 s^{-1} at the exit of the nozzle), the viscosity of the ABS and PPSU neat and fiber reinforced resins decreases with increase in deposition temperature while that of PEKK and fiber reinforced PEKK is not as temperature dependent but still influences volumetric throughput. The viscosity of neat PEKK decreases by 6% while that of the fiber reinforced PEKK decreases by only 4% [15] when the temperature is increased from 375 °C to 390 °C. In comparison, the viscosity of neat ABS and PPSU decreases by approximately 55% with increase in the processing temperature. Addition of carbon fiber to the neat resin increases the overall viscosity of all materials at the deposition temperatures [15,18]. The viscosity of fiber reinforced ABS and PPSU increases by 65% and 300% respectively [14,18].

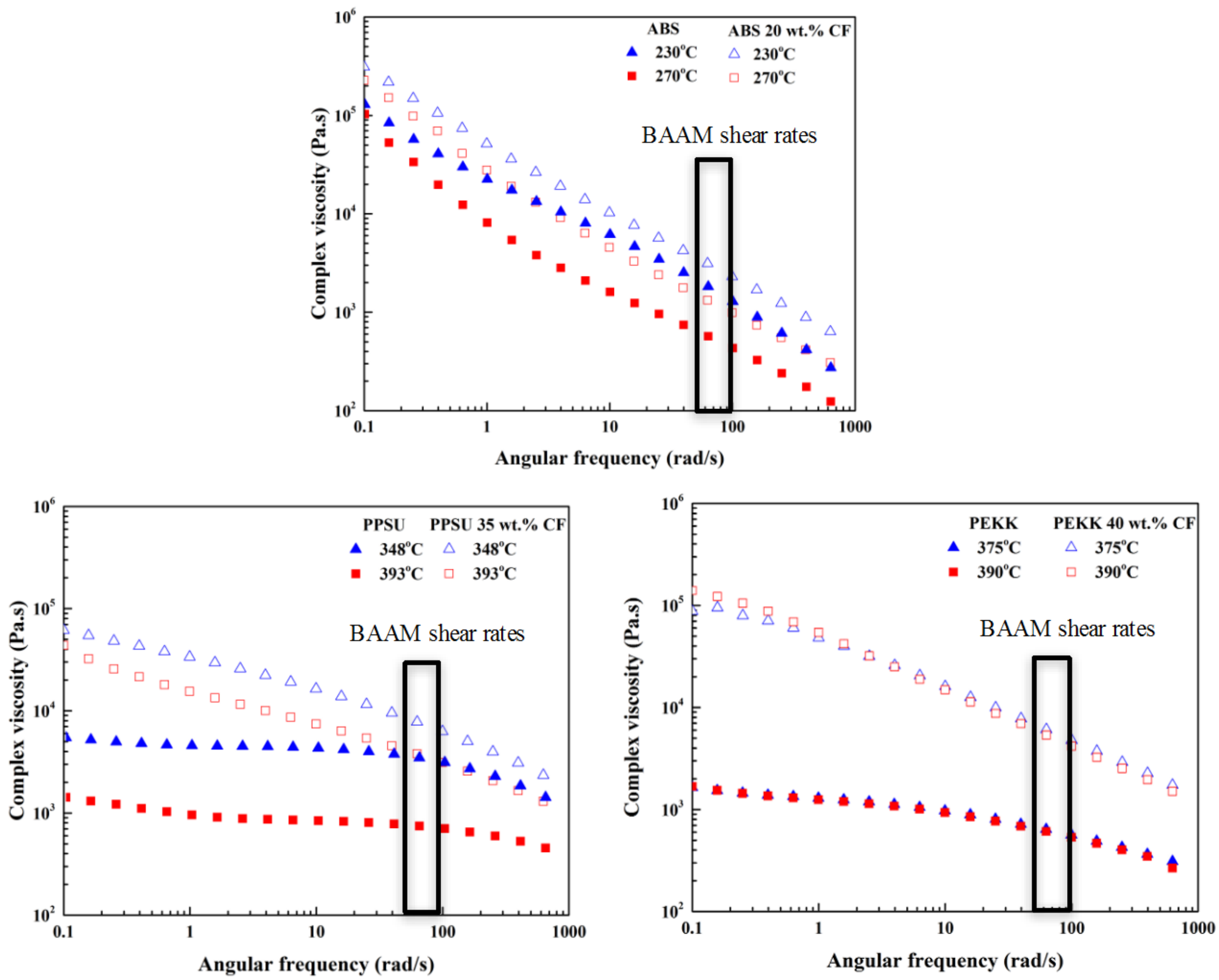

Figure 2. Viscosity of ABS, PPSU and PEKK composites as a function of temperature and angular frequency

To determine if the material will flow through the nozzle, the viscosities of the materials in the shear rates of interest are used to calculate the pressure-drop in the nozzle and at the exit of the nozzle (Table 3). The total pressure-drop in the nozzle is then compared to the maximum system pressure (P_{max}) on the BAAM system (6.89 MPa) to determine if the material will extrude (pass) or not (fail).

Table 3. Calculated nozzle pressure-drop conditions as well as model prediction status for ABS, PPSU and PEKK composites on BAAM at T_{dep}

	ABS	ABS	20%CF ABS	20%CF ABS
T_{dep} (°C)	230	270	230	270
ΔP_{nozzle} (MPa)	1.46	0.49	5.78	4.01
ΔP_{exit} (MPa)	0.41	0.12	1.34	0.88
ΔP_{total} (MPa)	1.87	0.61	7.12	4.89
Model prediction	Pass	Pass	Fail	Pass

	PPSU	PPSU	35%CF PPSU	35%CF PPSU
T_{dep} (°C)	348	393	348	393
ΔP_{nozzle} (MPa)	1.79	0.51	11.59	4.94
ΔP_{exit} (MPa)	0.72	0.2	3.72	1.52
ΔP_{total} (MPa)	2.51	0.71	15.31	6.46
Model prediction	Pass	Pass	Fail	Pass

	PEKK	PEKK	40%CF PEKK	40%CF PEKK
T_{dep} (°C)	375	390	375	390
ΔP_{nozzle} (MPa)	0.84	0.79	6.67	5.29
ΔP_{exit} (MPa)	0.32	0.3	1.98	1.48
ΔP_{total} (MPa)	1.16	1.09	8.65	6.77
Model prediction	Pass	Pass	Fail	Pass

According to the model predictions (Table 3), all the neat resins for ABS, PPSU and PEKK pass the pressure-driven extrusion criteria on the BAAM system. The total pressure required to extrude the neat resins is lower than P_{max}. Experimentally, ABS has been successfully extruded at these temperature on BAAM which further validates the model. Extrusion of neat PPSU and PEKK has not been attempted on BAAM; however, the model predicts that they would flow through the nozzle at the desired volumetric flow rate.

Addition of carbon fiber to the neat resin is preferred because fiber reinforced composites have a lower coefficient of thermal expansion (CTE) by an order of magnitude. Reducing the CTE with the use of fiber reinforced polymers minimizes the shrinkage as the part cools from the deposition temperatures to ambient temperatures and results in significantly reduced part distortion [4]. The pressure-driven flow model proposed predicts that the fiber reinforced composites of ABS, PPSU and PEKK fail to extrude at the lower deposition temperature for each material. At the higher deposition temperature; however, the model predicts that all the fiber reinforced composites can be successfully extruded.

Note that the majority of the pressure required for extrusion occurs in the long nozzle region prior to the exit diameter. In the nozzle region, the shear rate is much lower (~30 – 40 s^{-1}) due to the larger diameter, resulting in a higher viscosity in this region than experienced at the exit. Table 3 lists the pressure calculated in each region of the nozzle for the material systems and predicts that the lower temperature setting for 20% CF ABS (230 °C) would exceed the system pressure of 6.89 MPa, while the higher temperature setting would successfully extrude. Likewise, the extrusion print criteria model predicts that fiber reinforced PPSU would fail to extrude on BAAM at 348 °C while 40 wt.% CF-PEKK would fail to extrude at 375 °C.

The model agrees with experimental trials regarding extrusion on BAAM of the fiber reinforced composites. All of the candidate materials (20% CF ABS, 35% CF PPSU and 40% CF PEKK) have been successfully extruded on the BAAM system at the higher deposition temperatures (i.e. “pass”), but struggled to meet the desired flow rates at the lower deposition temperatures (i.e. “fail”). In practice, when depositing 35 wt.% CF-PPSU on BAAM at 348 °C, the material did extrude, but the flow was discontinuous and could not meet the desired flow rate. However, when the deposition temperature was increased to 393 °C, the flow through the nozzle was continuous and matched the desired flow rate. The viscosity of CF-PPSU is reduced by a factor of ~2 when increasing the temperature from 348 °C to 393 °C in the shear rate region of interest to BAAM (10-100 s^{-1}). Increase in deposition temperature for fiber reinforced PEKK does not have a significant effect on temperature as it did for CF-ABS and CF-PPSU and this is reflected in the pressure-drop calculations in the model. Although, the viscosity of CF-PEKK decreases by only a factor of 1 when temperature is increased from 375 to 390 °C, at 390 °C, 40% CF PEKK passes with a total pressure of 6.77 MPa which is very close to the maximum system pressure of 6.89 MPa.

Conclusions and future work

With increased utilization of polymer-based 3D printing systems for functional end-use components, several new high-performance thermoplastics are being explored. This paper presents an approach for screening potential polymer feedstock using a rheological/thermo-physical model on extrusion-based AM platforms. Initial studies with the pressure-driven extrusion criteria indicate that this model can be a useful tool for identifying appropriate printing conditions such as the deposition temperature as well as for guiding compositional changes associated with material development. This pressure-driven extrusion criteria is only the first step toward a more holistic approach of understanding the complex rheological and thermo-physical property interactions associated with extrusion-based 3D printing, and the model will certainly continue to develop. Future work will involve evaluating the pressure-driven extrusion model on FFF and DW AM systems and further experimental work to verify the validity of the model.

Acknowledgements

Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

References

[1] I. Gibson, D.W. Rosen, B. Stucker. Additive Manufacturing Technologies. 2009.

[2] E. Sachs, M. Cima, J. Cornie, D. Brancazio, J. Bredt, A. Curodeau, T. Fan, S. Khanuja, A. Lauder, J. Lee, S. Michaels. Three-Dimensional Printing: the Physics and Implications of Additive Manufacturing. Annals of the CIRP. 42 (1993) 257–260.

[3] C. Holshouser, C. Newell, S. Palas, L. Martin, C. Duty, L. Love, V. Kunc, R. Lind, P. Lloyd, J. Rowe, R. Dehoff, W. Peter, C. Blue. Out of Bounds Additive Manufacturing. Advanced Materials Processes. 171 (2013) 15–17.

[4] L.J. Love, V. Kunc, O. Rios, C.E. Duty, A.M. Elliott, B.K. Post, R.J. Smith, C. Blue. The importance of Carbon Fiber to Polymer Additive Manufacturing. Journal of Materials Research. 29 (2014) 1893–1898.

[5] L.J. Love. Utility of Big Area Additive Manufacturing (BAAM) for the Rapid Manufacture of Customized Electric Vehicles. ORNL Technical Report. 2014.

[6] B.N. Turner, R. Strong, S.A. Gold, A review of melt extrusion additive manufacturing processes: I. Process design and modeling. Rapid Prototyping Journal. 20 (2014) 192–204.

[7] B.N. Turner, S.A. Gold. A review of melt extrusion additive manufacturing processes: II. Materials, dimensional accuracy, and surface roughness. Rapid Prototyping Journal. 21 (2015) 250–261.

[8] M.R. Talagani, S. Dormohammadi, R. Dutton, C. Godines, H. Baid, F. Abdi. Numerical Simulation of Big Area Additive Manufacturing (3D Printing) of a Full Size Car. SAMPE Technical Conference (2015) 27–36.

[9] C. Duty, C. Ajinjeru, V. Kishore, B. Compton, N. Hmeidat, X. Chen, P. Liu, A. Hassen, J. Lindahl, V. Kunc, A Viscoelastic Model for Extrusion-Based 3D Printing of Polymers What Makes a Material Printable?. Journal of Manufacturing Processes. Submitted (2017).

[10] C. Duty, C. Ajinjeru, V. Kishore, B. Compton, N. Hmeidat, X. Chen, P. Liu, A. Hassen, J. Lindahl. A Viscoelastic Model for Evaluating Extrusion-Based Print Conditions. Solid Freeform Fabrication Symposium, 2017.

[11] C. Duty, V. Kunc, B. Compton, B. Post, D. Erdman, R. Smith, R. Lind, P. Lloyd, L. Love. Structure and Mechanical Behavior of Big Area Additive Manufacturing (BAAM) Materials. Rapid Prototyping Journal. (2016).

[12] V. Kishore, C. Ajinjeru, A. Nycz, B. Post, J. Lindahl, V. Kunc, C. Duty. Infrared preheating to improve interlayer strength of big area additive manufacturing (BAAM) components. Additive Manufacturing 14 (2017) 7–12.

[13] C. Ajinjeru, V. Kishore, Z. Sudbury, C. Duty, J. Lindahl, A. Hassen, B. Post, L. Love, V. Kunc. The influence of rheology on melt processing conditions of fiber reinforced polyetherimide for Big Area Additive Manufacturing. SAMPE Technical Conference, Seattle, 2017.

[14] C. Ajinjeru, V. Kishore, X. Chen, J. Lindahl, Z. Sudbury, A.A. Hassen, V. Kunc, B. Post, L. Love, C. Duty. The Influence of Rheology on Melt Processing Conditions of Amorphous Thermoplastics for Big Area Additive Manufacturing (BAAM). Solid Freeform Fabrication 2016, 754–761.

[15] V. Kishore, X. Chen, C. Ajinjeru, A.A. Hassen, J. Lindahl, J. Failla, V. Kunc, C. Duty. Additive Manufacturing of High Performance Semicrystalline Thermoplastics and their Composites. Solid Freeform Fabrication 2016, 906–915.

[16] V. Kishore, C. Ajinjeru, C. Duty, A. Hassen, J. Lindahl, P. Liu, V. Kunc. Rheological Characteristics of Fiber Reinforced Poly (ether ketone ketone) (PEKK) for Melt Extrusion Additive Manufacturing. SAMPE Technical Conference, Seattle, 2017.
[17] J. Aho. Rheological Characterization of Polymer Melts in Shear and Extension : Measurement Reliability and Data for Practical Processing. PhD. Dissertation. 2011.
[18] C. Ajinjeru, V. Kishore, P. Liu, J. Lindahl, A. Hassen, V. Kunc, C. Duty. Determination of Melt Processing Conditions for High Performance Amorphous Thermoplastics for Big Area Additive Manufacturing (BAAM). Additive Manufacturing. Submitted (2017).