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High performance poly(etherketoneketone) (PEKK) composite parts fabricated using Big Area Additive Manufacturing (BAAM) processes

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Materials Science and Technology Division
Advanced Manufacturing Office

HIGH PERFORMANCE POLY(ETHERKETONEKETONE) (PEKK) COMPOSITE PARTS FABRICATED USING BIG AREA ADDITIVE MANUFACTURING (BAAM) PROCESSES

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This CRADA NFE-16-06056 was conducted as a Technical Collaboration project within the Oak Ridge National Laboratory (ORNL) Manufacturing Demonstration Facility (MDF) sponsored by the US Department of Energy Advanced Manufacturing Office (CPS Agreement Number 24761). Opportunities for MDF technical collaborations are listed in the announcement "Manufacturing Demonstration Facility Technology Collaborations for US Manufacturers in Advanced Manufacturing and Materials Technologies" posted at http://web.ornl.gov/sci/manufacturing/docs/FBO-ORNL-MDF-2013-2.pdf. The goal of technical collaborations is to engage industry partners to participate in short-term, collaborative projects within the Manufacturing Demonstration Facility (MDF) to assess applicability and of new energy efficient manufacturing technologies. 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.

ABSTRACT

ORNL collaborated with Arkema Inc. to investigate poly(etherketoneketone) (PEKK) and its composites as potential feedstock material for Big Area Additive Manufacturing (BAAM) system. In this work thermal and rheological properties were investigated and characterized in order to identify suitable processing conditions and material flow behavior for BAAM process.

1. HIGH PERFORMANCE POLY(ETHERKETONEKETONE) (PEKK) COMPOSITE PARTS FABRICATED USING BIG AREA ADDITIVE MANUFACTURING (BAAM) PROCESSES

This technical collaboration project (MDF-TC-2016-081) started on February 2, 2016 and was completed on August 31, 2016. The collaboration partner is Arkema, Inc. which is a large global chemicals and materials manufacturing company that operates 28 facilities in 16 states, with a U.S. headquarters and Research and Development Center in King of Prussia, Pennsylvania. The rheological characteristics of Arkema's poly(etherketoneketone) (PEKK) high performance thermoplastic polymers relevant to BAAM processing was evaluated in this work. Thermal and rheological testing helped to identify appropriate conditions by which PEKK can be extruded for potential use in large additively manufactured structures.

1.1 BACKGROUND

Big area additive manufacturing (BAAM) is a large scale polymer extrusion-based system developed at the Manufacturing Demonstration Facility (MDF) at Oak Ridge National Laboratory (ORNL). This system, with a build volume of 6 x 2.4 x 1.8 m, uses pelletized feedstock of thermoplastics and fiber reinforced composites to print parts at temperatures as high as 510ºC. Such capabilities have enabled the use of this system to investigate printing of parts with new high performance materials that can be used in different advanced applications.

Arkema Inc. supplies products and develops materials for many key markets, with a particular strategic emphasis on providing solutions to diverse global trends. One of the key global trends Arkema Inc. is developing and providing solutions for is lightweight materials. Arkema Inc. is particularly focused on strong research and development initiatives in the use of thermoplastic materials and composites, including resin materials for parts fabricated by melt extrusion-based Additive Manufacturing (AM) processes. Arkema Inc. manufactures PEKK, a high performance semi-crystalline thermoplastic material that finds applications in the automotive, aerospace, oil and gas sectors. In order to determine the feasibility of using Arkema Kepstan™ PEKK on the BAAM system, the objective of this project was to determine suitable processing conditions for these materials and characterize their flow behavior for extrusion based processes. Thermal and rheological analysis of various grades of Kepstan™ PEKK (shown in Table 1) were performed to determine the melt processing temperature range, and understand the effect of shear, temperature, processing environment and time on the viscosity of the chosen materials.

Table 1. Kepstan™ pellets grades

Kepstan™ Series	Neat	Glass Fiber (GF) Reinforced	Carbon Fiber (CF) Reinforced
6000 (pseudo amorphous)	6002 6003	6010G30 (30% weight GF)	
7000 (semi-crystalline)	7002		
8000 (semi-crystalline)	8001		8010C30 (30% weight CF) 8010C40 (40% weight CF)

1.2 TECHNICAL RESULTS

1.2.1 Thermal Analysis

Thermal characterization involved Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) analysis of these materials to identify the upper and lower processing temperature limits respectively. Fig.1 (a-c) represent data for TGA analysis done in air at a heating rate of 10°C/min for 6000, 7000 and 8000 series pellets, respectively. The results indicated the materials to be stable up to at least 500°C without significant degradation and release of volatiles (less than 2% weight loss).

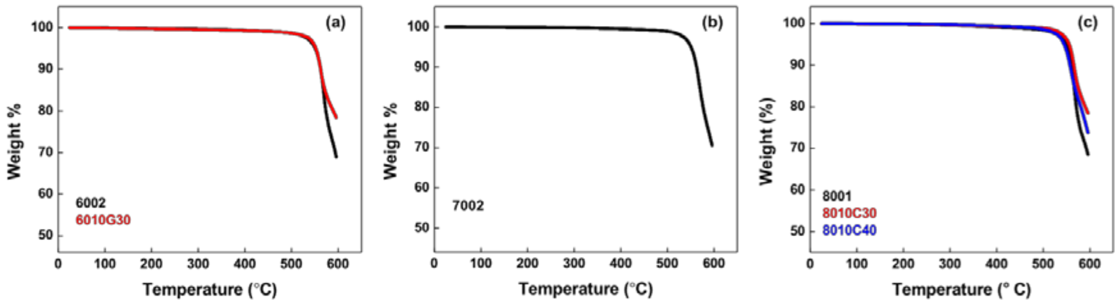
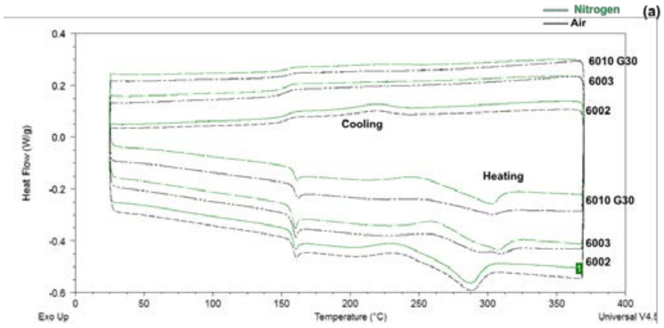


Fig. 1. TGA analysis of (a) 6000 grades, (b) 7000 grade and (c) 8000 grades.

Fig. 2 (a-c) represents DSC thermograms for the seven grades of PEKK for tests conducted in air and nitrogen. The samples were heated at the rate of 10°C/min, cooled at 5°C/min and re-heated at 10°C/min. The plots represent the second heating cycle and the first cooling cycle. From this analysis, the pseudo amorphous 6000 grades had a glass transition temperature (T_g) of 158-159°C, the semi-crystalline 7000 grade PEKK had a T_g of 161°C and a peak melting temperature (T_m) of 335°C and the 8000 series grades had T_g of 156°C - 158°C and T_m of 361-362°C. There was no significant difference in T_g and T_m data obtained for tests in air and nitrogen environments.



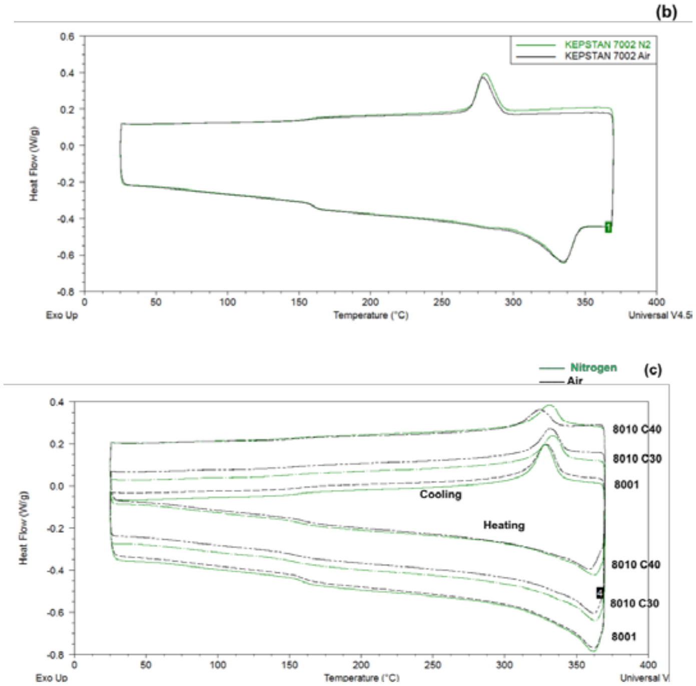


Fig. 2. DSC analysis of (a) 6000 grades, (b) 7000 grade and (c) 8000 grades.

1.2.2 Rheological Analysis

From the obtained lower (T_g or T_m) and upper (degradation onset temperature) processing temperature limits, rheological experiments were performed on a TA Instruments DHR-2 instrument fitted with 25 mm parallel plate geometry. Table 2. summarizes the rheological tests performed, focusing on the semi-crystalline grades.

Table 2. Rheological analysis

Kepstan™ Series	Test Environment	Test Performed
7000	Nitrogen	Frequency sweep – 1 hr time sweep - frequency sweep (at T_m +15°C, i.e., 350°C)
8000	Nitrogen	Frequency sweep – 1hr time sweep - frequency sweep (at T_m +15°C, i.e., 375°C)
	Air	Frequency sweep at T_m + 15°C, T_m + 30°C, T_m + 45°C (i.e., 375°C, 390°C, 405°C)

Fig. 3 (a-d) represents frequency sweep tests (628- 0.1 rad/s), followed by one-hour time sweep (at 1 rad/s) and another frequency sweep (628- 0.1 rad/s) for the 7000 and 8000 grades samples in nitrogen environment. The plots indicate the variation in storage modulus (G'), loss modulus (G") and complex viscosity (η^*) with angular frequency. All the grades exhibit shear thinning, with the extent increasing with the addition of fillers. For the oscillatory time sweep tests, the increase in viscosity with time for 1 hr at 1 rad/s is shown by the vertical data points. From fig 3a, for the 7000 grade, there is an increase in viscosity of the material after 1 hour at all frequencies, with the increase being the highest (~70%) at the lowest frequency measured (0.1 rad/s). For 8001 grade, the same trend was observed but the increase at 0.1 rad/s was ~ 230%. It was observed that addition of fillers increased the viscosity values as well as the increase in viscosity after time sweep. At 0.1 rad/s, for 30 wt.% CF, the increase was ~ 1120% and for 40 wt.% CF, the increase was ~ 1730%. Note that the data points in some ranges with high noise have not been shown in the plots. This type of rheological analysis provides useful insights on how the material behavior changes under shear, with time and with the addition of fillers. This can be useful to identify the process parameters that can better control the rheological properties during extrusion processing and also be a useful indicator for understanding scenarios such as extruder clog that might arise over a period of time.

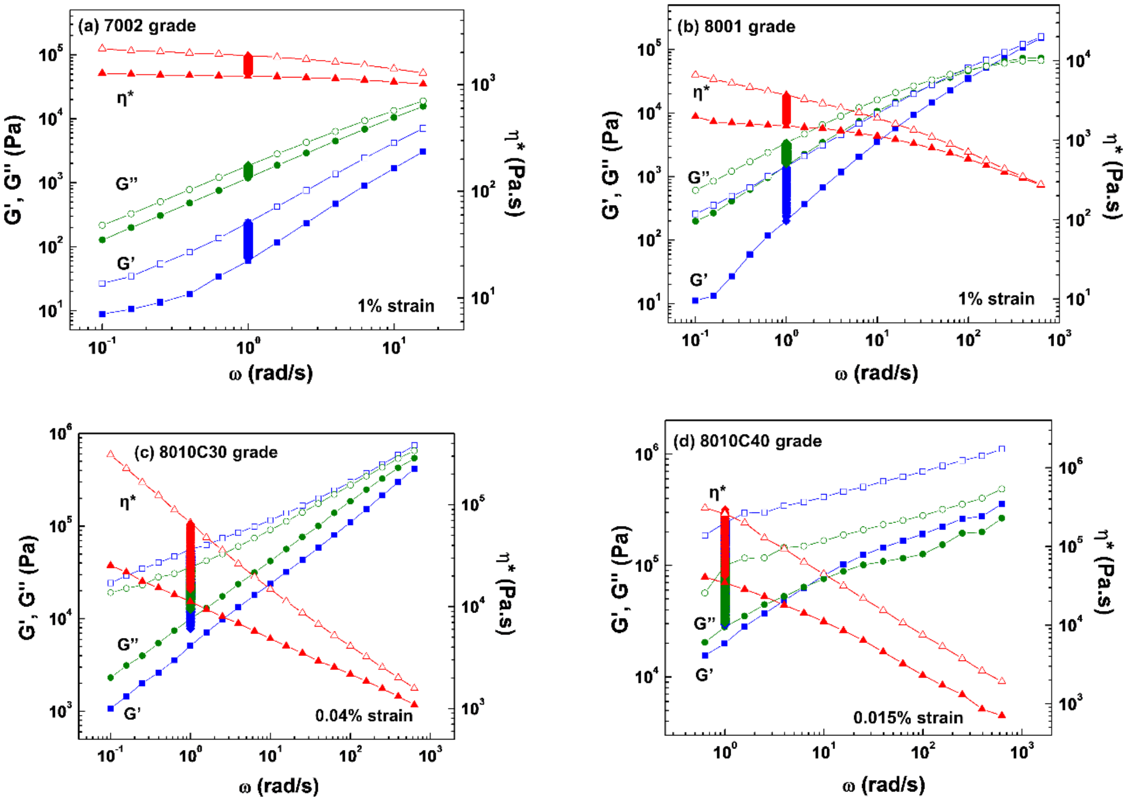


Fig. 3. Frequency-time-frequency sweep in nitrogen at T_m + 15°C for (a) 7002 grade, (b) 8001 grade, (c) 8010C30 grade and (d) 8010C40 grade. Filled symbols indicate first frequency sweep parameters (▲ complex viscosity η*, ■ storage modulus G' and ● loss modulus G") and open symbols indicate frequency sweep after time sweep.

Fig. 4 indicates viscosity variation with temperature in air for 8000 series samples at three different temperatures with 15°C increments (375°C, 390°C and 405°C). This was done as an attempt to understand the effect of temperature on these grades in air. It can be observed that the addition of fillers increase viscosity of the material at all frequencies and both neat as well as filled grades exhibit shear thinning. For the 8001 grade (neat), temperature does not significantly impact viscosity at all frequencies and the dependence of viscosity on temperature is also low for the filled grades at high frequencies. At low frequencies, there is an increase in viscosity at temperature above 400°C for the 8010C40 grade. This can be due to some structural changes induced at such temperatures in air. This study indicates shear to be a better parameter to vary viscosity during extrusion (if required) than temperature changes.

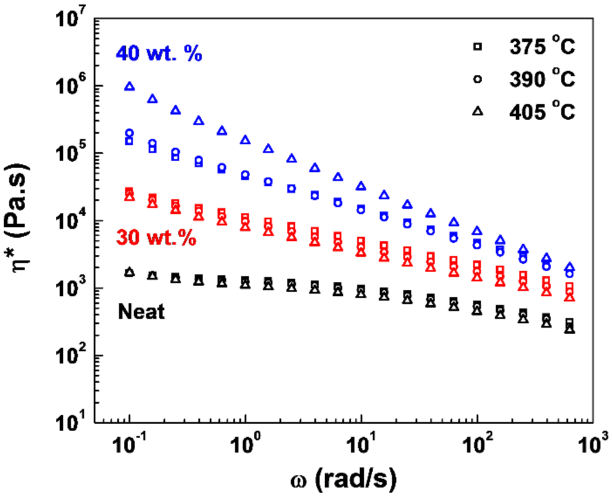


Fig. 4. Variation of viscosity with temperature for 8000 grades (neat and carbon fiber filled) [1].

1.3 IMPACTS

The impact of a successful BAAM-produced high temperature polymer/composite structure is the ability to rapidly manufacture customized parts in a short period of time and at lower cost relative to current manufacturing that uses high cost metal alloys. The challenge in using PEKK in additive manufacturing is its higher price relative to thermoplastics such as polylactide (PLA) and acrylonitrile butadiene styrene (ABS) commonly used in Fused Deposition Modeling (FDM)-type processes. However, materials such as PLA and ABS simply cannot match the performance of PEKK. This is especially true when a printed part must have high mechanical properties and can operate at elevated temperature. Semicrystalline PEKK has a tensile strength of ~20 MPa (3000 psi) at 175°C. The BAAM system is now using reinforced amorphous acrylonitrile butadiene styrene (ABS) material with glass transition temperature of 105°C. If high temperature operation is a requirement, the typical thermoplastics used in AM are not feasible options.

The advantages of PEKK over current large parts made using metal alloys include its much lighter weight and easier handling, as well as more rapid manufacture and potential recyclability of the polymer (or composite). The thermal and rheological results obtained in this phase showed the feasibility of using Arkema PEKK high performance thermoplastic polymers for BAAM process. The polymer extrusion conditions and ranges was successfully identified. The polymer system can be used in BAAM system and investigation of the fabrication of dimensionally stable large additive manufactured structures should be performed. Based on this study, carbon fiber reinforced PEKK shows potential for 3D printing of large structures. Given this material’s enhanced capabilities for high temperature strength, wear resistance, fatigue resistance, flame/smoke/toxicity rating, and chemical resistance, it may be appropriate for bearings, seals, and other internal components of large equipment such as wind turbine rotor hubs or pump casings. There may also be interest in large scale, lightweight structures for aerospace applications and construction of high temperature molds for manufacture of engineering polymers.

1.4 CONCLUSIONS

From the thermal and rheological studies performed in this work, suitable processing temperature range has been identified for PEKK and its composites. It has also led to an understanding of the flow behavior of the chosen grades of PEKK and the process parameters that are critical to extrusion based processes.

1.5 REFERENCES

1. V. Kishore, X. Chen, C. Ajinjeru, A. Hassen, J. Lindahl, J. Failla, V. Kunc, and C. Duty. "Additive Manufacturing of High Performance Semicrystalline Thermoplastics and Their Composites." *Proceedings of the Solid Freeform Fabrication Symposium*, Austin, TX (August 8-10, 2016).

2. PARTNER BACKGROUND

Arkema, Inc. is a global chemicals and materials manufacturing company that operates 28 facilities in 16 states, with a U.S. headquarters and Research and Development Center in King of Prussia, Pennsylvania. Its parent company, Arkema S.A., is headquartered in Colombes, France. Arkema supplies products and develops materials for many key markets, with a particular strategic emphasis on providing solutions to address five emerging global trends: bio-based materials from renewable raw materials; new and alternative energy sources; water management; organic and micro-electronics, and lightweight materials. In this latter area, Arkema is particularly focused on strong research and development initiatives in the use of thermoplastic materials and composites, including resin materials for parts fabricated by melt extrusion-based Additive Manufacturing processes.