RECYCLING CARBON FIBER FILLED ACRYLONITRILE-BUTADIENE-STYRENE FOR LARGE FORMAT ADDITIVE MANUFACTURING

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Abstract

The recovery, recycling, and reuse of large format additive manufacturing (LFAM) composite scrap material as a secondary feedstock material is essential for the feasibility of large-scale AM (LSAM) sustainability. Carbon fiber reinforced acrylonitrile butadiene styrene (CF-ABS) was recycled and used as a secondary LSAM feedstock material to understand printability behaviors against that of virgin feedstock materials. Each material was printed on the Big Area AM system. Rheological and preliminary fiber length were evaluated. Rheological characterization was used to determine if the recycled feedstock materials were viable for printing. Fiber analysis was performed to gain understanding of fiber degradation in the recycling process. By successfully characterizing the impact of incorporating secondary feedstocks in large-scale AM, a pathway can be defined for further reducing material waste and improving AM sustainability.

Background

In recent years, the shift towards circular economic principles and zero-waste manufacturing has given rise to increased awareness of wastefulness, the lifecycle of consumer products, and the environmental actions needed for sustainable disposal plans. Large format additive presents an excellent technology to further the understanding of manufacturing with recycled polymer materials. Focusing on fiber-filled polymer materials, also known as fiber reinforced plastics (FRP), is important due to their use in products created by automotive[1], mold and tooling[2], and defense industries. The American Chemical Council reports that plastic materials can be 50% of a car's volume and fiber-filled polymer materials are often utilized in aerospace and defense systems as well[3]. Plastics and many fiber-filled polymer composites are a prevalent aspect of everyday life and used widely across industries and applications – used in everything from packaging, electronics, and automobiles[4]. The versatile use of plastics has resulted in a 500% increase in global plastic production and is expected to increase to 850 million tons per year by 2050, compared to the 348 million tons produced between the years 1950 and 2017 [5,6]. Because carbon fiber-filled and reinforced materials are utilized in a multitude of applications for a range of industries, we must consider the environmental and energy demands needed to keep up with the growing industrial demand of these materials. Specifically, the demand for carbon fiber as a whole is expected to reach 194 kilotons for utilization in carbon fiber reinforced plastics (CFRP) by the year 2022 [7] where the energy demand to make carbon fiber is 183-286 MJ/kg and produces 31 kg of carbon dioxide equivalents per kilogram of carbon fiber manufactured [8].

Researching and understanding carbon fiber-reinforced materials recyclability for additive manufacturing is imperative to the future of the additive manufacturing industry. Additive manufacturing (AM) as an industry has been growing rapidly due to its ability to meet the technical challenge of more complex and highly customizable parts, especially for composite materials[9]. Many of the limitations surrounding the study of recyclability in AM is due to the restrictions on size and volume of many AM technologies, where small-scale AM recycling has been explored but there are currently no studies on recycling fiber-filled materials for large format additive manufacturing (LFAM). The development of Big Area Additive Manufacturing (BAAM) systems by Oak Ridge National Laboratory (ORNL) and Cincinnati Inc. showed that these large format additive manufacturing systems could print 10-20 times larger than typical small-scale systems without the use of filament, but rather with a single-screw extrusion method and utilization of pelletized material as feedstock[10].

Large format additive manufacturing is useful to the developments of molds and tooling. Molds and tooling are used across multiple application areas such as: automotive, aerospace, construction, energy, and defense industries[10,11]. Disposing of molds and tooling of such large sizes can create large volumes of composite waste due to the sizes of parts able to be printed on LFAM systems. Typically, the composite materials for molds and tooling consist of a thermoset resin system – which cannot be recycled [12]. Utilizing manufacturing and recycling techniques for carbon fiber-filled thermoplastics, to produce molds and tooling, can help to alleviate the environmental burden caused by the thermoset resin waste of large parts. Instead, recovering a large part made from thermoplastic resin and converting it, through mechanical recycling, can allow for an increased lifespan of the materials used in these applications.

This research explores the printability and fiber length distribution of a common AM material, carbon fiber acrylonitrile-butadiene-styrene, with 20% weight fraction of carbon fiber (CF-ABS). This recycled material was studied as a new feedstock material for the BAAM system at the Oak Ridge National Laboratory. This study allows for new understanding of the printability for secondary recycled feedstock materials for large format additive systems.

Materials and Methods

Material Conversion and Re-pelletization

The first step of recycling CF-ABS (ELECTRAFIL ABS 1501 3DP) for large-format additive manufacturing is to convert recovered waste parts made from virgin material into new pellets. Parts were milled into flakes using a standard CNC mill. Once CF-ABS shavings were collected, the material shavings were sent to Techmer PM to be converted into new pellets via re-blending in a twin-screw extrusion system. Once fully re-melted, the new recycled material was pelletized, where the pellet was approximately 2.5mm in diameter and approximately 3mm in length.

Rheological Properties

Rheological behavior of the virgin CF-ABS, recycled CF-ABS, and neat ABS was assessed with a Discovery Hybrid Rheometer-2 (DHR-2), where parallel plate geometry with a diameter of 25mm was utilized. The rheological testing was performed at 250°C, which is the standard BAAM printing temperature for these materials. The materials were tested with an oscillatory frequency sweep in air at a frequency range of 0.1-628 radians per second and applied strain of 0.1%. The frequency ranges were chosen to capture material behavior within the printing nozzle. The applied strain chosen to fall within the materials' linear viscoelastic region.

The gap height between the plates was 1.5mm. The materials were dried at 80°C for 4 hours before experimentation.

Printing Parameters

Samples of virgin CF-ABS and recycled CF-ABS were printed on the BAAM system at Oak Ridge National Lab's Manufacturing Demonstration Facility. Each box was 0.61m x 0.61m x .03m with a 12.7mm wall thickness and consisted of 80 layers. The boxes, seen in Figure 1, were printed at 250°C and 45 RPM, with a 0.76cm nozzle diameter and a 90 second layer time. The printed samples were allowed to cool for 15 minutes on the print bed, maintained at 100°C, before removal to reduce probability of part warpage.

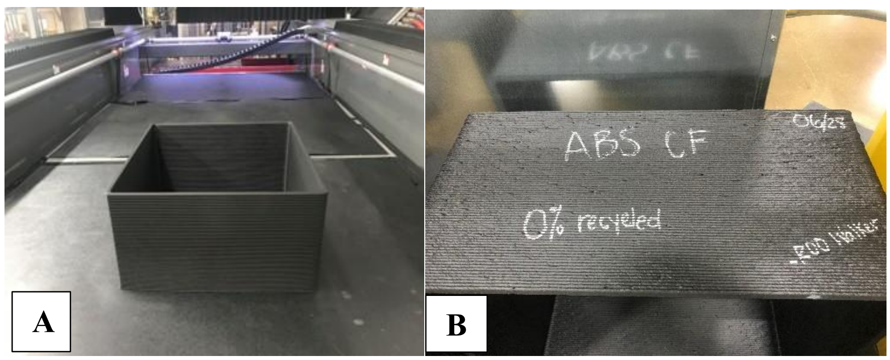

Figure 1. A – Recycled CF-ABS Printed Sample, B – Virgin CF-ABS Printed Sample

Fiber Recovery and Analysis

Fiber imaging was done for recycled CF-ABS pellets and recycled CF-ABS printed material and compared to baseline data of non-recycled pellets [13]. Acetone digestion was used to isolate the carbon fiber from the ABS polymer matrix[14]. For the acetone digestion, 5 grams of material was added to approximately 30ml of acetone. The pelletized material was added straight to the acetone, whereas a 5-gram chunk of the printed material was cut from the center of the wall to be added to the acetone. This solution was mixed for 30 seconds using to a vortex mixer and then allowed to sit for 24 hours. After 24 hours, approximately 20ml of acetone was added to the CF-ABS-acetone solutions and mixed for 30 seconds with a vortex mixer. The solutions were then applied to microscopy slides and given time for the acetone to evaporate from the slide surface and imaged on a Keyence Optical Microscope with 50x total magnification.

The images were processed using the Fiji processing package for ImageJ [15,16]. The image was converted to an 8-bit image and the lighting of the image was adjusted to allow for more distinct contrast between the fibers and the image background. The fibers in the image were then measured using an automatic measurement program designed to measure the length of rod-like geometries [17]. These measurements were reported in pixel size and then converted to micrometers using the number of pixels that the scale bar represents. These measurements were then weight averaged to determine average fiber length of their respective material. For each material system, over 2000 fibers were imaged and measured, per ISO 22314 standards [18].

Results and Discussion

Rheological Properties

The flow behavior of three materials; virgin CF-ABS, neat ABS, and recycled CF-ABS, were evaluated using frequency sweep tests within the linear viscoelastic region to determine if the recycled material exhibited complex viscosity similar to that of the virgin and neat counterpart materials. The shear rates of interest were 30-40 s^{-1} which are the shear rates experienced inside the printing nozzle and 100-200 s^{-1} which are the shear rates experienced as the material exits the printing nozzle. The increase is shear rates from nozzle entrance to nozzle exit are due to the narrowing of diameter at the exit of the nozzle. The tested materials are observed to be shear-thinning at the tested frequencies, 0.1-628 rads/s. There is a reduction in the complex viscosity for recycled CF-ABS when compared to virgin CF-ABS but remains within the known printability window that is represented by the lower bound of neat ABS and the upper bound of the virgin CF-ABS, as seen in Figure 2. Neat ABS and virgin CF-ABS do not necessarily represent an absolute boundaries of printability but instead provides a printability window where pressure driven extrusion flow is likely to occur[19,20]. The region created by the virgin CF-ABS and neat ABS defines an operable printing window, where materials within the bounds of the two sets of complex viscosities are also printable at the observed BAAM shear rates[20].

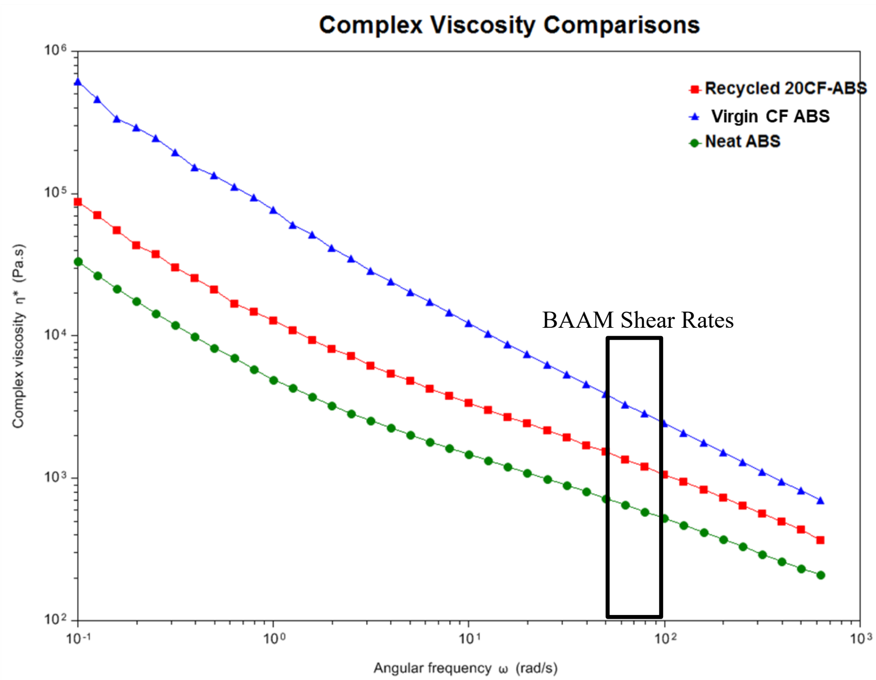

Figure 2. Complex viscosity of Neat ABS, Virgin CF-ABS, and Recycled CF-ABS as a function of temperature and angular frequency

Fiber Recovery and Analysis

Carbon fiber added to thermoplastics greatly influences the observed mechanical properties of printed part and observing the change in fiber length allows for inference about mechanical behavior in recycled part. Fiber length weighted averages were calculated [21]. Weighted fiber average assesses the influence that longer fibers have on the overall distribution whereas basic number average is primarily influenced by the number of small fibers within the measured population. The weighted average fiber length in virgin CF-ABS pellets has been observed to be 212.60 µm. In parts printed with virgin CF-ABS the weighted average fiber length has been observed as 196.32 µm, demonstrating a 7.96% decrease in fiber length after printing [13]. Figure 3 shows the fiber length distribution of recycled CF-ABS pellets. The weighted average fiber length was observed as 83.71 µm. Figure 4 shows the fiber length distribution for the printed part made from recycled CF-ABS. The weighted fiber average fiber length observed was 75.27 µm. Figure 5 shows the combined fiber length distributions for recycled and virgin CF-ABS materials.

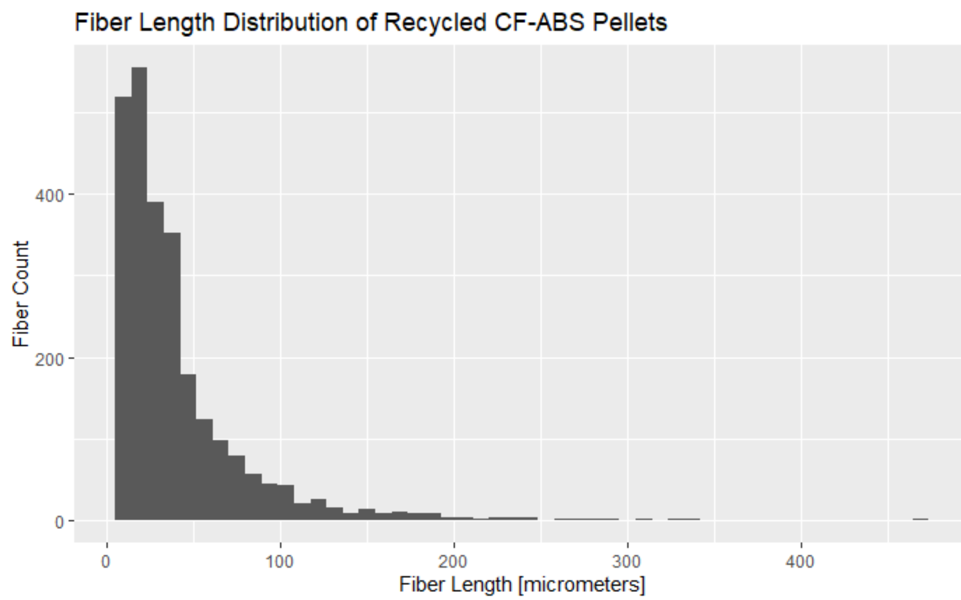

Figure 3. Fiber length distribution for recycled CF-ABS pellets

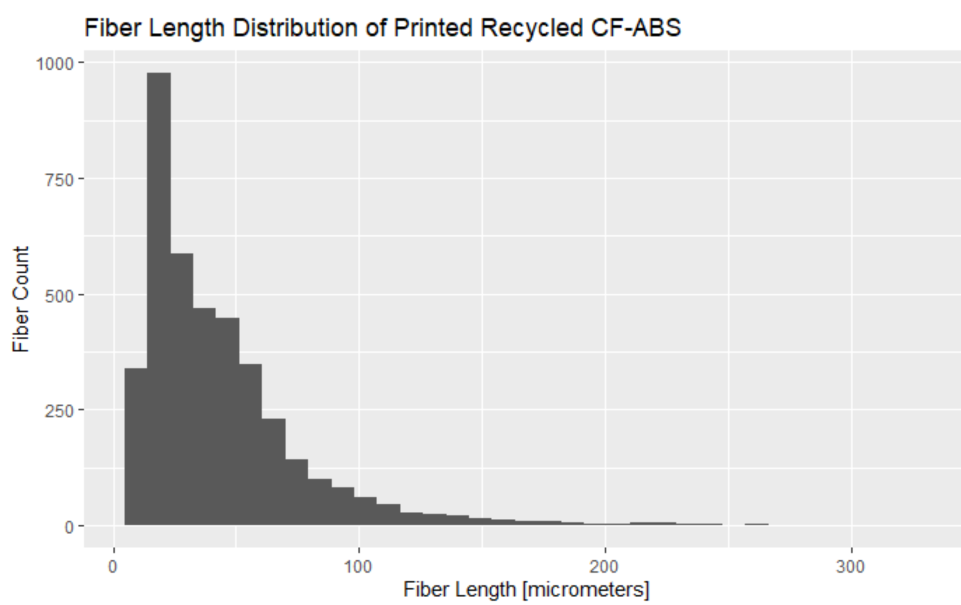

Figure 4. Fiber length distribution of printed recycled CF-ABS

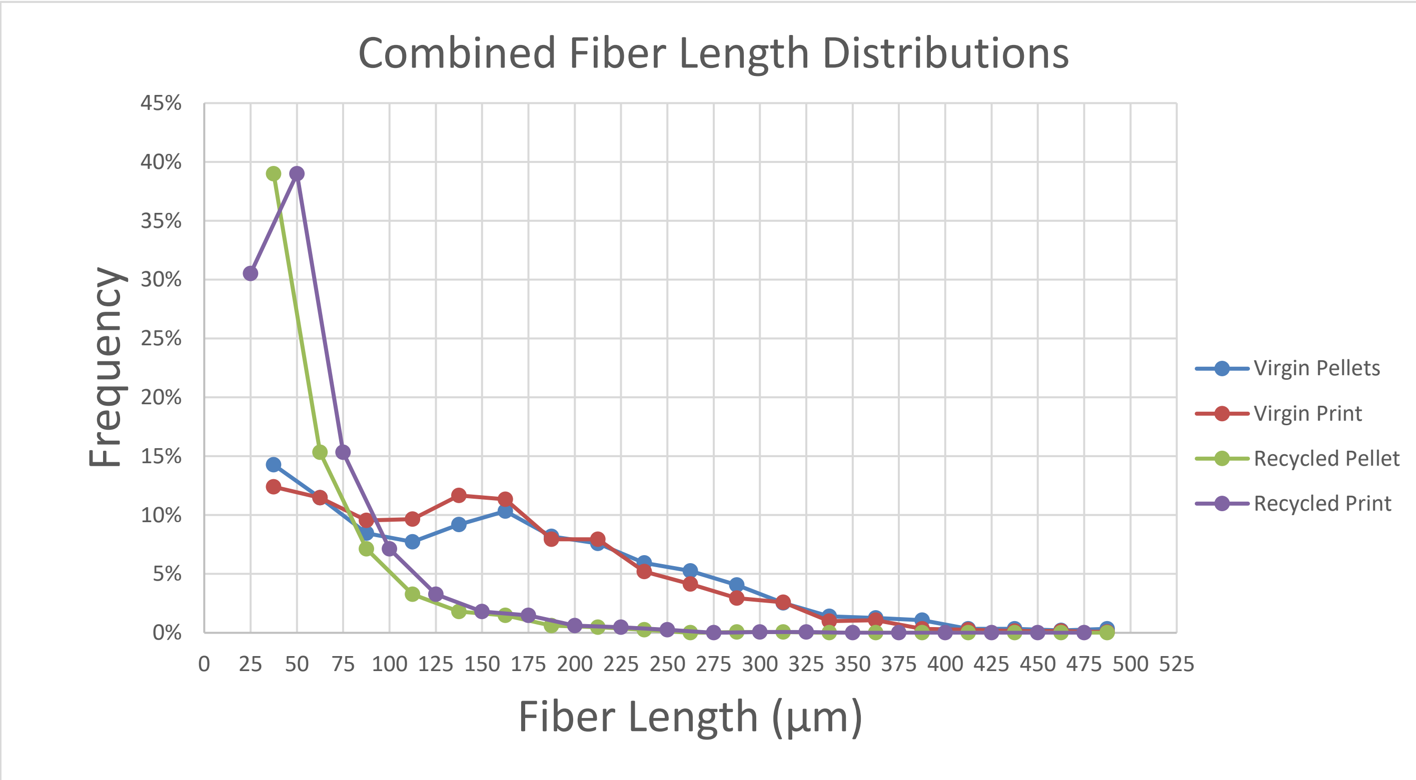

Figure 5. Combined weighted average fiber length distribution

The process to convert virgin CF-ABS printed material into recycled feedstock is a mechanically intensive process that introduces a large amount of mechanical degradation to not only the polymer matrix but also the carbon fiber. When comparing the recycled CF-ABS pellets to the virgin CF-ABS pellets, there is an 86.9% decrease in fiber length that is occurring during the conversion process. The change in weighted average fiber length from recycled CF-ABS pellet to recycled part is 10.6%. The aspect ratio of fibers within a composite material is one of the most important parameters when considering the overall tensile strength of a part made with fiber-filled composites. Fiber aspect ratio is the ratio of the length of a fiber over the diameter of the fiber and as this ratio increases, the tensile properties of a composite will also increase until it hits a maximum tensile strength [22]. The average aspect ratio of the non-recycled composite printed material is 28, where the diameter of the fiber is 7 µm [13]. Whereas the average aspect ratio of the printed recycled material is 10.75, where the diameter of the fiber is 7 µm. The decrease in weighted average fiber length and the decrease of the average fiber aspect ratio alludes to potential degradation of tensile strength in the recycled CF-ABS printed parts..

Conclusions and Future Work

This research describes the ability to successfully recover and recycle CF-ABS at least one time for use in large-format additive manufacturing systems. Virgin parts were converted into recycled feedstock materials through milling into shavings, re-melting, and re-pelletization into feedstock. The flow behavior was observed to determine the materials printability on a large-format AM system. The rheological studies showed that while the complex viscosity of the recycled material decreased in comparison to the virgin counterpart, the flow behavior was still within a region that allowed for printability when compared to virgin CF-ABS and neat ABS. The recycled material was printed and there were no observed issues during the printing processing. The fiber length was observed in both the recycled pellets and the recycled printed part. Fiber analysis showed there was 86.9% decrease in fiber length in the recycled CF-ABS pellets when compared to their virgin CF-ABS counterparts and a 10.6% decrease in fiber length within the prints made with recycled material when compared to carbon fiber lengths typically seen in in printed virgin carbon fiber materials used in large format additive manufacturing. Further research is needed to quantify the mechanical behavior of parts made from recycled CF-ABS and to observe how the change in fiber length may influence the overall mechanical behavior of a recycled part.

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