

LARGE-SCALE ADDITIVE MANUFACTURING WITH REACTIVE POLYMERS

John Lindahl¹, Ahmed Arabi Hassen¹, Stian Romberg¹, Ben Hedger², Peter Hedger Jr.², Mike Walch², Tim Deluca², Wes Morrison², Seokpum Kim¹, Alex Roschli¹, David Nuttal¹, John Czachowski¹, Brian Post¹, Lonnie Love¹, Vlastimil Kunc¹

¹Manufacturing Demonstration Facility, Oak Ridge National Laboratory
NTRC II, 2370 Cherahala Blvd, Knoxville, TN 37932

²Magnum Venus Products (MVP)
1862 Ives Ave., Kent, WA 98032

ABSTRACT

The focus on large-scale polymer Additive Manufacturing (AM) has previously been on thermoplastic materials. However, Magnum Venus Products (MVP) along with researchers at Oak Ridge National Laboratory's (ORNL) Manufacturing Demonstration Facility (MDF) are introducing a unique AM system capable of depositing reactive polymers in a large format. The system's footprint is 4.88 m (16ft) x 2.44 m (8ft). The benefits of printing with reactive polymers rather than thermoplastic polymers include reduced dependence on temperature control of the process, chemical reactions across the bead-to-bead interfaces, and increased toolpath flexibility that is currently unattainable with existing large-scale systems. This flexible AM system can be used with a variety of polymers, and pre-processing and post-processing operations will be performed outside of the printer on a removable print bed. Examples of printed structures and machine capabilities leading to improved productivity of AM equipment are presented herein.

1. INTRODUCTION

Large-scale polymer Additive Manufacturing (AM) is a recent technological development in the field of AM. To date the primary polymeric resins used in large-scale AM have been thermoplastic, both amorphous and semi-crystalline [1,2,3,4]. While these materials have been very successful, they do come with some limitations. In traditional large-scale AM, thermoplastic is melted and deposited by a single screw extruder on a 3-axis gantry [2]. Structures are built by repeatedly depositing molten plastic onto the previously deposited layer. The temperature gradient between the previous layer and the currently deposited layer, in cases of very large printed structures, could lead to warping [2], and in some cases this warping can lead to disbonding between layers [5,6]. This stress buildup limits the size of a given machine's build envelope based on an extruder's maximum volumetric output. Furthermore, the added

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>). *CAMX Conference Proceedings. Dallas, TX, October 15-18, 2018. CAMX – The Composites and Advanced Materials Expo*

weight of the extruder and insulating accessories necessary to impart heat to the material limit the gantry's ability to accelerate quickly. Greater speeds would correlate to increased AM production rates and encourage more widespread adoption of AM technology [2].

Polymer AM is primarily used in non-structural or semi-structural applications [1,2,3,4,5]. Aside from prototyping and shape demonstrations, the technology is used in industry for manufacturing of custom jigs, fixtures and tools where only material stiffness is required to satisfy most application requirements [1,2,4]. The strength of the interface between the layers in thermoplastic material AM process limits the use of AM parts in load bearing structure [4]. Thermoset layered manufacturing can alleviate this problem by using polymers that will fully cross-link between layers, and not rely on partial fusion of polymer chains as in the case of thermoplastic printers [7]. Thermoset materials can be printed at room temperature or at slightly elevated temperature, which reduces the thermally-induced residual stresses and deformations allowing for printing large structures [7]. Thermoset printing is a promising alternative which addresses the thermal issues encountered by thermoplastic AM, as thermoset polymers do not require heat to behave viscoelastically. Research has been successfully conducted using reactive thermoset polymers in small-scale printing [8,9,10,11]. One of the most accessible small-scale thermoset printing technologies is Direct Ink Writing (DIW) [8,9]. In this process, a polymer resin is mixed with a catalyst which begins the cross-linking process unique to thermosets. In this paper we introduce a new AM system for reactive polymers. The system is designed to have a large print volume of 4.88 m (16ft) x 2.44 m (8ft) x 1.02 m (40 in) for in height length, width, and height respectively. Being the first of its kind to include a thermoset mixing nozzle, remote volumetric pumps, and large-area printing capability, this machine will enable researchers to probe the feasibility and desirability of large-scale thermoset printing using reactive polymers.

2. SYSTEM DESCRIPTION

The large scale reactive polymer additive system developed through a collaboration between Magnum Venus Products (MVP) and Oak Ridge National Laboratory (ORNL) enables rapid manufacturing of large parts out of thermosetting resins. This innovative large-scale system provides solutions for some of the processing limitations in small scale reactive polymer systems, such as low feedstock volume, limited workspace size, in-situ changes in viscosity, added processing steps to obtain fully cured material, and the lack of purpose-built systems. Figure 1 shows the large scale reactive polymer additive system. The System consist of three major sections:

2.1 Resin Pumping Station

Unlike small scale systems all resin transfer systems are decoupled from the gantry system. Therefore, all the heavy pumping equipment used for deposition is located next to the machine and connected to the nozzle via relatively lightweight hoses. This design decision provides the added benefit of decreased weight in comparison to the screw extruder in large thermoplastic system. Consequently, print speed can be increased, reducing print time, increasing production rate, and ultimately making AM a more attractive option for full-scale production operations. The pump used in this system is a Patriot Chop Check transfer pump (model PAT-CCP-LS-0590). This pump is used for transferring raw non-catalyzed resin to a custom build Patriot resin

metering pump. The Patriot Chop Check pump can be provided in two different capacities, 19-liter (5-gallon) pails and 208-liter (55-gallon) drums. The Patriot Chop Check pump coupled with the metering pump provides consistent resin flow and fluid pressure to the deposition head. Catalyst is gravity fed from a 7.57-liter (2-gallon) reservoir to a Patriot Catalyst pump (model PAT-CP-0245). The two metering pumps are mounted together on a pump drive assembly arm that is moved up and down by a servo hydraulic actuator seen in Figure 1. By mounting the metering pumps together on the same arm, catalyst to resin ratios are controlled by adjusting the catalyst metering pump attachment points on the drive assembly arm. Due to the particular pump design by MVP equal amounts of resin are pumped during the upstroke and downstroke of the actuator. This gives consistent deposition of the mixed resin when building parts.

2.2 Deposition Head

In small scale systems, resin is mixed prior to the printing process (i.e. outside the printer). In this large-scale system, a unique nozzle design allows for mixing immediately prior to deposition, circumventing the curing and thickening issues associated with small scale reactive polymer systems. The resin and catalyst are both pumped to an Auto Pro Gun block (model CPC) where they are combined into one single fluid channel. The combined resin and catalyst go through a 22.86 cm (9 in) static mixing section. This provides adequate mixing of the resin and catalyst to ensure full cure is obtained in the deposited material. After mixing the catalyzed resin flows to the deposition nozzle. Within the deposition nozzle there is a shut off valve to ensure resin is deposited only when instructed to by the programmed toolpath. The deposition nozzle (see Figure 1) has an air controlled fast acting pneumatic system to rapidly raise and lower for X-Y travel moves when not depositing resin. Nozzles of various diameters ranging from 1.27 mm (0.05 in) to 10.16 mm (0.4 in) can be used on this system; however, currently for the preliminary system evaluation a nozzle diameter of 5.08 mm (0.2 inches) was chosen.

2.3 Gantry and Build Platform

The deposition head is attached to a gantry system capable of speeds up to 1.27 m/s (50 in/s) in X-Y motion. The printing speed is highly dependent on the fluid pressure and rheological characteristics of the material. The build platform for this system has a 4.88 m (16ft) x 2.44 m (8ft) footprint and can support printed structures up to 1.02 m (40 in) in height. The build platform consists of a stainless-steel substructure with precision machined aluminum platens. Each individual platen has a vacuum port to hold down the polyethylene build sheets from which fully cured parts can be easily removed for re-use of the build sheets. The build platform is capable of supporting up to 453.6 kg (1000 lb.) of deposited resin with minimal deflection. A unique feature unlike other large-scale AM systems, is an easily transferable build platform. This will allow for an option of using latent curing thermoset materials that would need to be cured at elevated temperatures in an oven.



Figure 1: Large scale reactive polymer additive system showing the build platform, resin pumping station, and deposition head system

3. FEEDSTOCK MATERIAL

Unlike thermoplastic additive systems the large scale reactive polymer additive system uses thermoset materials that do not require thermal energy input to process. Thermoplastics are rigid at room temperature. They require thermal energy and mechanical energy through shear to melt and process the material [3]. The thermoset resins that are used on the reactive polymer system are in a liquid state at room temperature and begin to cross-link only when exposed to the proper catalyst [7]. Deformations and residual stress build up should be reduced by utilizing thermoset materials. Polyester and vinyl ester base resin systems with peroxide catalysts to initiate curing are the current tested feedstock material for this system. These resins were chosen due to their tunable cure times and the ability to accept a wide variety of rheology modifiers, such as Nano clays, fumed silica, and glass fibers. Each of these rheology modifiers has a different impact on the resin system with the goal of turning the base resin into a highly shear thinning thixotropic material [7,8,9]. Figure 2 shows a print for a large vinyl ester hexagonal structure that will be used for determining mechanical material properties of this material system. Due to the speed of the system none of the layers seen in Figure 2 have gelled or cured. This shows that the resin has sufficient viscosity at a zero-shear state to support multiple layers of uncured resin. This is extremely important when moving to more complex geometries that have variable layer times. This will also help improve mechanical properties orthogonal to the build plane [7].

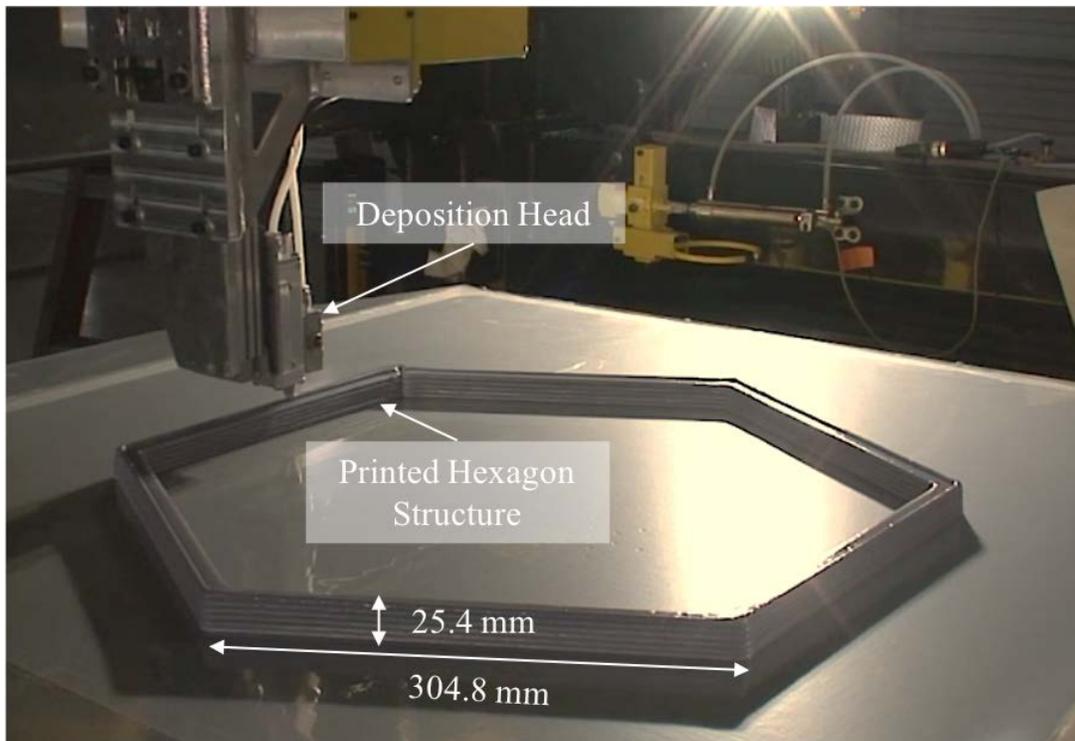


Figure 2: AM multi-layer hexagon printed with vinyl ester material

4. APPLICATIONS

This system can be used for fabrication of molds and dies for composite manufacturing. Molds and dies are a crucial element in the production process of durable, and high-quality composite

components [1]. This technology can be used for manufacturing different types of composite tooling ranging from out of autoclave tools such as Vacuum Assisted Resin Transfer (VARTM) and hand lay-up molds, to trim tools, joining molds, and to autoclave tools. These thermoset materials should also come in a lower cost point than their equivalent thermoplastic counterparts.

One of the most promising applications is manufacturing of cores for composite sandwich structures. These structures typically consist of two load bearing skins and a lightweight core. The skins are typically made of fiber reinforced composite or aluminum sheets. However, the core is a foam or honeycomb structure that is made usually of impregnated paper, plastic sheets, or aluminum sheets. The main function of the core is to transfer moderate load between skins in compression and shear modes. The honeycomb density is currently sized to accommodate the highest load experienced by the structure as the current technologies are limited to fabricating only uniform density honeycombs. Joining these sheets is difficult and time consuming. AM can uniquely and effectively address these limitations by printing variable density cellular structures tailored for each individual application, as shown in Figure 3. Tailored variable core structures has shown to meet or improve core mechanical performance used in sandwich composites, while reducing weight and material needed [12,13]. Large area reactive polymer additive manufacturing technology can generate lighter structures and consume less material, resulting in energy and cost savings for both manufacturers and end users. The example in Figure 3 is for an airfoil geometry that can be used in aircraft wings or wind turbine blade structures.

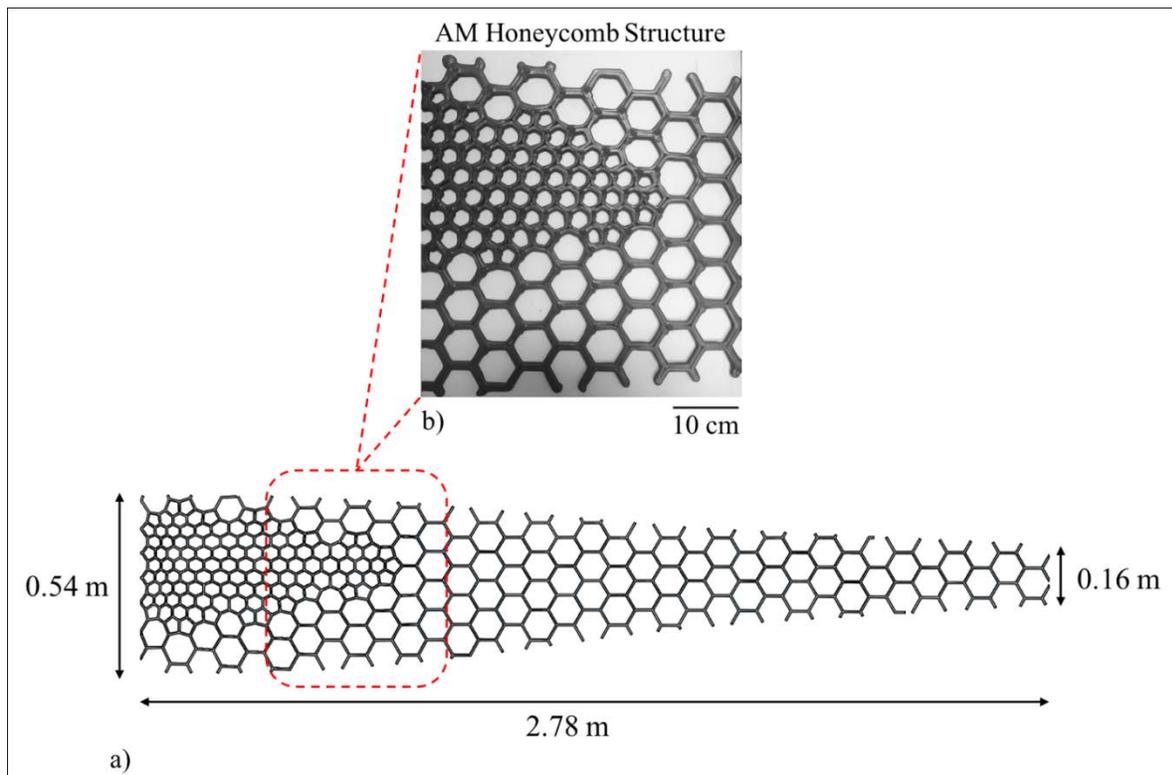


Figure 3: a) Schematic for the gradient infill pattern honeycomb structure, and b) Actual AM honeycomb structure using vinyl ester material

5. CONCLUSIONS

In summary, we have detailed and showed the first purpose-built large-scale reactive polymer additive manufacturing system. A fast gantry with a precision thermoset pumping system will allow exploration of a new space in polymer AM. The thermoset materials used by this system should be able to compete with thermoplastic AM parts, and it should permit new applications where strength and isotropic structure properties are required. Using liquid resin enables continuous complex toolpath solutions for building structures that would be difficult to use with thermoplastic materials. More research and development will be performed in order to improve the performance and functionality of the printer. Development of new material feedstocks for this printer is crucial.

6. ACKNOWLEDGEMENTS

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

7. REFERENCES

- [1] Kunc V, Hassen AA, Lindahl J, Kim S, Post B, Love L. Large Scale Additively Manufactured Tooling For Composites. 15th JAPAN International SAMPE Symposium and Exhibition. Japan; 2017.
- [2] Love, L.J., et al., The importance of carbon fiber to polymer additive manufacturing. *Journal of Materials Research*, 2014. 29(17): p. 1893-1898.
- [3] Ajinjeru K, Kishore V, Liu P, et al., Rheological Evaluation of High Temperature Polymers to Identify Successful Extrusion Parameters. *Solid Freeform Fabrication 2017*, Austin, TX; 2017.
- [4] Duty CE, Drye T, Franc A. Material Development for Tooling Applications Using Big Area Additive Manufacturing (BAAM). Oak ridge National Laboratory (ORNL); Manufacturing Demonstration Facility (MDF); 2015.
- [5] Hassen AA, and Kirka M, Additive Manufacturing: the Rise of a Technology and the Need for Quality Control and Inspection Techniques. *Materials Evaluation*, 2018.76(4): p. 438-453.
- [6] Compton B.G., et al., Thermal analysis of additive manufacturing of large-scale thermoplastic polymer composites. *Additive Manufacturing*, 2017. 17: p. 77-86.
- [7] Kunc V, Lee A, Mathews M, Lindahl J, et al., Low Cost Reactive Polymers for Large Scale Additive Manufacturing. *CAMX 2018*, Dallas, TX; 2018.
- [8] Lewis J.A., Direct Ink Writing of 3D Functional Materials. *Advanced Functional Materials*, 2006. 16(17): p. 2193-2204.
- [9] Compton B.G. and Lewis J A, 3D-Printing of Lightweight Cellular Composites. *Advanced Materials*, 2014. 26(34): p. 5930-5935.
- [10] Duoss E.B., et al., Three-Dimensional Printing of Elastomeric, Cellular Architectures with Negative Stiffness. *Advanced Functional Materials*, 2014. 24(31): p. 4905-4913.
- [11] Rios O., et al., 3D printing via ambient reactive extrusion. *Materials Today Communications*, 2018. 15: p. 333-336.

- [12] Kim S, Chen X, Dreifus G, et al., An Integrated Design Approach for Infill Patterning of Fused Deposition Modeling and its Application to an Airfoil. SAMPE 2017, Seattle, WA; 2017.
- [13] Kim S, Dreifus G, Beard P, et al., Graded Infill Structure of Wind Turbine Blade Core Accounting for Internal Stress in Big Area Additive Manufacturing. CAMX 2018, Dallas, TX; 2018.