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Advances in Binder Jet Additive Manufacturing

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Manufacturing Science Division
Advanced Materials and Manufacturing Technologies Office

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ABSTRACT

Binder Jetting is a powerful additive manufacturing technology due to its low cost and wide range of types of materials it can shape. The industry partner ExOne has a range of binder jet products for applications such as casting tools, composite layup tools, single-alloy metal components, and more. As such, research and development is of high interest in the area of specialized binders for each type of material, processing technology that improves reliability and quality, and materials to enhance the performance of the final parts. Thus, this work focuses on developing novel binders for sand tools and metal prints, new capabilities in multi-material printing, and build monitoring and correction. The result of this work includes a novel binder system that makes binder jet sand stronger than concrete while still being water soluble, a casting binder that is environmentally friendly and produces better surface finishes on castings, and a binder for metals that reduces the residual carbon.

Statement of Objectives

The objectives of the work are as follows:

1. Develop a binder replacement for casting binders which is more environmentally friendly than Furan and Phenolic and reduces off gassing to produce higher value castings.
2. Develop a binder for metals that leaves behind less carbon after burnout.
3. Develop binders that improve the processing of metals either as a sintering aide or low-carbon binder.
4. Develop a machine-learning system that recognizes build defects
5. Develop multi-material printing capability for advanced components.
6. Develop a polymer coating system for sand that allows for spray-coating, composite layup, and washout of the coating and printed sand.

Benefits to the Funding DOE Office's Mission

Binder jet additive manufacturing is a low-cost method for producing parts with enhanced geometries that are less energy intensive to manufacturing and potentially reduce energy usage of the machine they are integrated into (due to light weighting, enhanced heat transfer, etc.). For transportation, being able to produce complex composite structures through washout tooling is an major opportunity to reduce the weight of vehicles. For metal manufacturing, having a method of manufacturing that produces high-purity alloys in complex geometries could replace energy-intensive processes such as metal injection molding and investment casting. Further, multi-material printing has the potential to unlock new device types that perform significantly more efficiently than current, single-material manufacturing allows.

Technical Discussion of Work Performed by All Parties

The three main tasks are proposed toward enhancing binders for binder jet AM are minimizing offgassing, minimizing charring or residual elements left by the polymer, and exploring binders to enhance final part functionality. The basic steps in each of these tasks include a review of polymer systems and their fundamental properties related to the goal of each task, selection of commercially available polymers and modifying their rheology for ink-jetting, characterizing the green part strength of the printed parts, and final characterization of the desired properties.

A summary of each task is as follows:

For Task 1, a binder was developed that reduced surface roughness on castings.

For Task 2, a binder was developed that reduced the amount of residual carbon on printed metal parts.

For Task 3, binders were developed with metals incorporated, however, a path forward was not identified due to toxicity issues.

For Task 4, a machine learning algorithm was developed and demonstrated to be able to recognize short spreading in builds and correct for them.

For Task 5, a multi-material printer was developed, however, integration and troubleshooting was not accomplished due to funding limitations.

For Task 6, a polymer system was developed that allows for the spray-coating of printed sand, layup of composite on the sprayed mold, and washout of the mold with water.

Full details of the work are detailed as follows:

Task 1: Casting Binders

Binder jetting is a highly versatile technology with applications in many different spaces including metal matrix composites, single alloys, and sand preforms for casting or washout tooling. Current binders used in sand mold production include Furan and Phenolic, which are known to be toxic to the environment. However, Furan and Phenolic binders are sought after for their strength at temperature and relatively low off-gassing during the casting process. Furan and phenolic binder systems have been developed for binder jetting and have been utilized since the early stages of the technology by ExOne and other companies to produce low-volume sand molds for metal casting. The first task in this CRADA was to develop special binders for binder jetting of sand that are low-toxicity and reduce off-gassing during casting of metals into the printed sand molds.

The development of the casting binder involved a series of experiments with multiple, commercially available polymers mixed in varying ratios with solvents and rheology modifiers. The polymer, carrier solvent, and modifiers constitute the binder system. The criteria involved in developing new binders are determined by the printhead itself in terms of chemical compatibility and rheology of the fluid. In terms of chemical compatibility, there are some data known about piezo-electric printheads and fluids which can cause corrosion. Further, the viscosity and surface tension requirements for the ExOne printheads is available. Thus, using these criteria, the list of possible binders to explore is made.

After procuring candidate binders, they are mixed with sand to determine bonding strength. The mixtures are cast into bars and their breaking strengths measured on a 4-pt. bend test. These results aren't always accurate; however, it is currently the best know method for screening binders without printing each individual system.

The binder system with the highest strength in the prescreen was called "Binder A" and was used to print a number of sand molds, which were used to cast aluminum propellors. The propellors were scanned for geometric accuracy and measured for surface finish. Surface finish is an indication of binder offgass – a smoother cast surface indicates less binder off gassing during casting, while a rougher cast surface indicates more binder off gassing. Needless to say, smoother surfaces on castings are desirable and also indicate less porosity within the metal. The results of the casting showed more deviation in geometry with the new binder than with the Furan. However, surface roughness measurements between the two types of casting revealed a 17% decrease in roughness with the use of the new binder. This is due to the new polymer's better stability at casting temperatures.

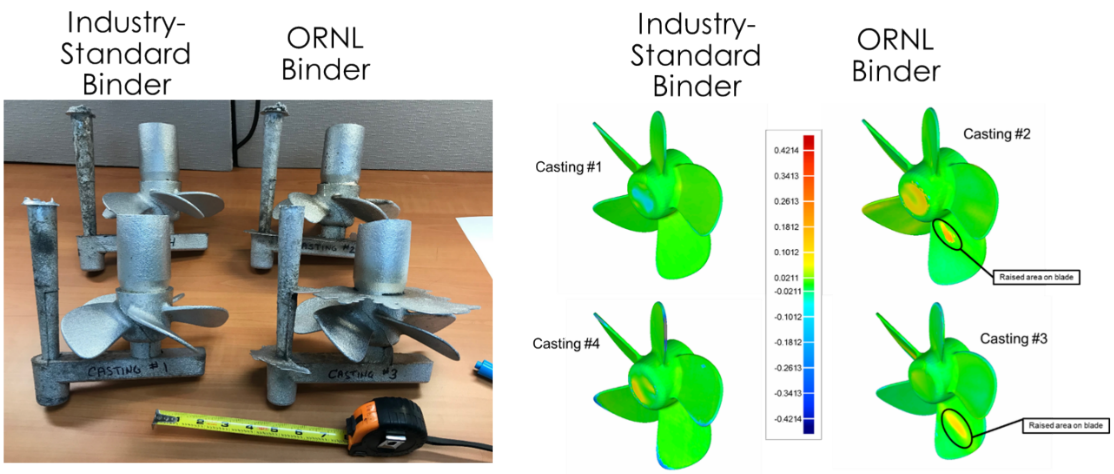


Figure 1: Castings made with printed molds (left) surface measurements of castings (right)

Table 1: Roughness measurement comparing castings made with Binder A and Furan

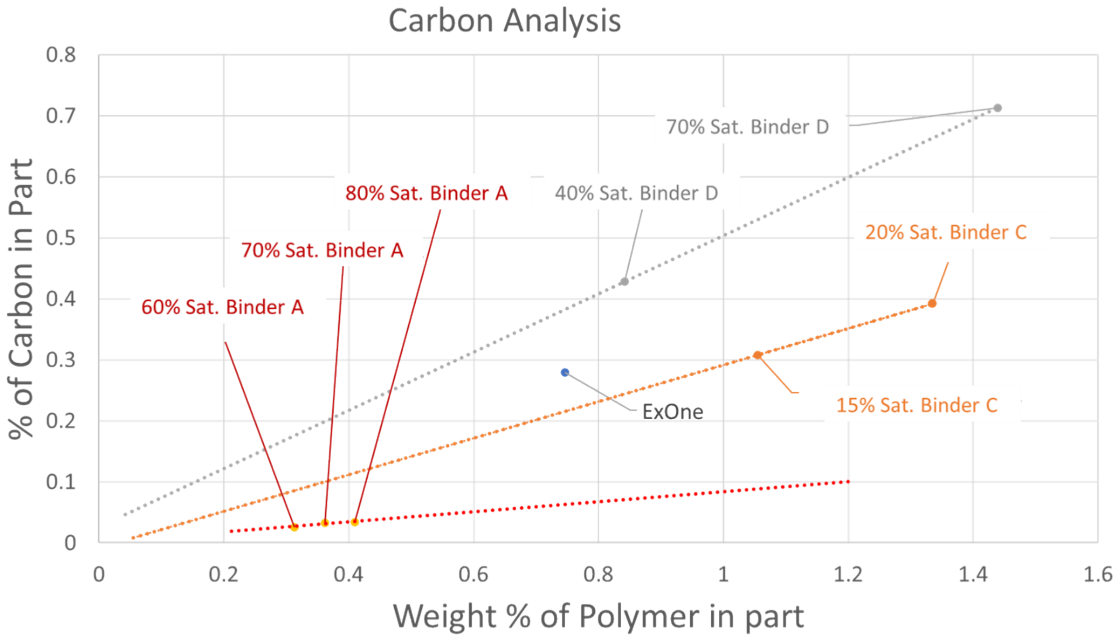
Measurement (micro-inch)	1	2	3	Avg.
Binder A	896.929	797.638	785.866	826.8
Furan	1045.512	816.97	1137.24	999.9
Sand Cast [1]				500-1000
Investment Cast [1]				63-125

The result of this R&D task was the licensing of the new casting binder and exploration by the industry partner. It is anticipated that environmental laws will soon preclude the use of Furan and Phenolic in the casting industry, so the potential exists for wide-spread adoption of this binder in the future.

<u>Task 2: Low Carbon Binder for Metals</u>

Binder jetting is also commonly used to produce single-alloy metal parts through the shaping of metal powder into a "green" preform that is then sintered or consolidated to a fully dense part. This is not unlike metal injection molding (MIM), which is used to produce millions of parts each year in the US. One issue with both binder jetting and MIM is the amount of carbon left behind after the polymers are burned out prior to sintering. The carbon shifts the composition of the metal powder and can reduce the performance of the alloy. Thus, the second task in this CRADA was to develop new binder systems for binder jetting that reduces the amount of carbon left behind during pyrolysis.

To approach this challenge, candidate binders were selected based on 1) their decomposition profile and 2) their commercial availability. Decomposition profile is a factor of a number of polymer characteristics, such as carbon-bond types. Thermogravimetric Analysis (TGA) and other data were either taken or referenced to identify appropriate candidate binders. Ultimately, three different polymers were chosen, procured, and mixed to form Binders A, B, and C. Each of these binders were printed on an ExOne binder jet printer at varying saturations and then analyzed for residual carbon after binder burnout. It was found that Binder D had the highest amount of carbon, Binder C had similar carbon levels to the ExOne binder, and Binder A had significantly lower carbon levels, even at high saturations. Further analysis showed that the decomposition of Binder A produced more carbon-containing molecules than others, which is enabled by strategic bond-types from the base-polymer molecule. Below is a graph of the binder types and the residual carbon levels.



The binder system has been licensed and is still being studied by the industry partner.

Task 3: Binders that add functionality to metal alloys

The purpose of this task was to develop a method for incorporating potentially useful metals or sintering aides into the binder and see the effects on printed parts in terms of reducing distortion, increasing density, or other benefits. The metal-loaded binders were developed, however, toxicity and corrosivity became an issue with their use in the binder jet printer.

The materials selected for this task were nickel and cobalt. These materials are useful as sintering aides for many alloys and can also serve to improve green part strength by bonding powder particles together during curing. Several binders were developed that incorporated alloying metals for the purpose of adding functionality in terms of improving sintering or infiltration performance (see table below). Nickel was added in the form of salt ion to a co-polymer (two monomers combined into a polymer) to create a stable solution. This type of approach is ideal for binder systems as other approaches (like nano-particle suspensions) can clog the inkjet nozzles. Figure 2 displays the different binders that were developed.

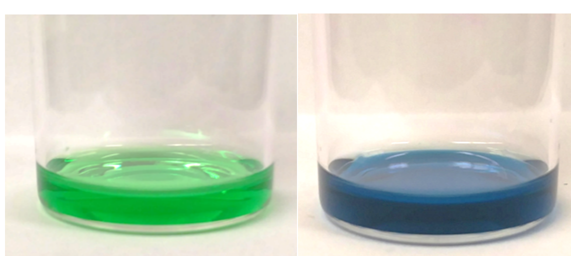


Figure 1: Nickel Salt with 0.52Ni/g binder (left) and Nickel Salt with Additive and 1.3g Ni/g Binder (right)

Ultimately, one of the binder systems was tested on an ExOne X1 lab system, but the toxicity and corrosiveness of the metal prevented further studies. The study resulted in a patent disclosure on metal ions attached to co-polymers in a binder system suitable for binder jetting.

Task 4: Machine learning system

An area of opportunity for all AM systems is the ability to monitor each layer of the print for defects and adjust process parameters as needed to ensure part quality (among many other uses for build monitoring). This task was focused on using ORNL's Peregrine technology to train a machine learning system to identify print defects during binder jet prints and adjust build parameters to correct for them. The build error of focus for this task was a phenomena called "short-spreading," which is what happens when an insufficient amount of powder is fed to the layer, and a gap in the layer results after spreading. The software was trained to identify this type of build error and correct for it by adjusting hopper settings to provide more powder on the following layers. Once the error was identified as corrected, the software stopped the adjustments. The work has resulted in a journal publication and follow-on discussions about licensing and further development of build-correction technologies for binder jetting.

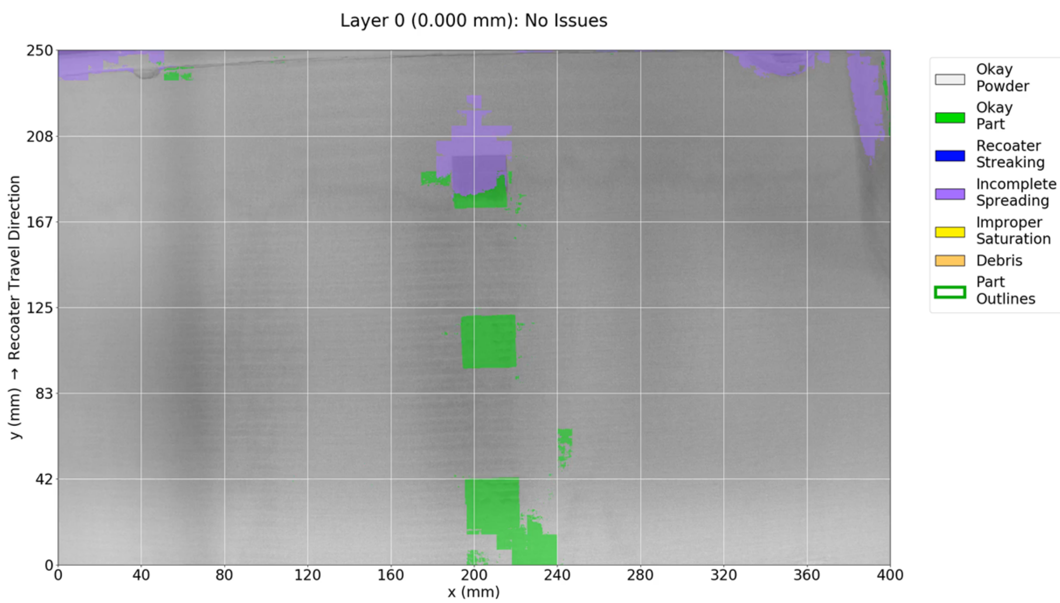


Figure 2: Build error identification screen demonstrating the identification of short-spreading

Journal Publication

L. Scime, D. Siddel, S. Baird, V. Paquit. "Layer-wise anomaly detection and classification for powder bed additive manufacturing processes: A machine-agnostic algorithm for real-time pixel-wise semantic segmentation." *Addit. Manuf.* 36 (2020): 101453. https://doi.org/10.1016/j.addma.2020.101453.

Task 5: Multi-material powder bed

To achieve multi-material powder deposition, the approach proposed here is to utilized powder spreading, binding, and vacuuming technology in unison to produce multi-material artifacts from powdered materials. A machine has been designed and built at the MDF (Figure 8) to achieve the selective deposition of powders via a modified binder jet process and will be integrated, refined, and demonstrated during this work. The machine consists of a chassis made from an optics table, a powder handling system which deposits and collects powder, a build axis which holds the build box and moves the build stage up and down, a printhead that moves on 2 axis, a printhead station for wiping and maintenance, among other major systems. Although the majority of the system components are in place, limited testing has been performed to verify each subsystems functionality, and no work has been done to integrate all systems to work together. Thus, not only is further testing and redesign is needed on the individual component level, but systems integration and testing will be needed as well. Overall, this task constitutes the majority of the work to be done during this LDRD.

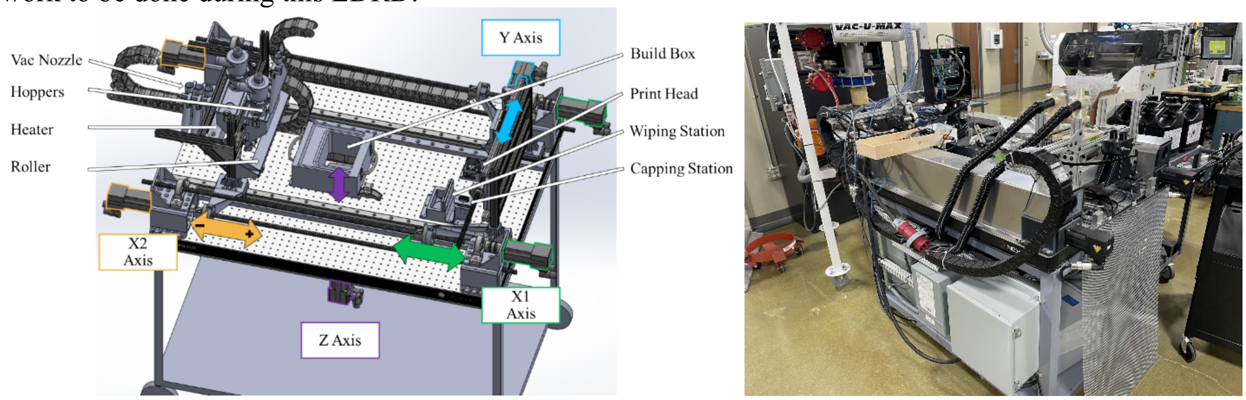


Figure 3: System Design (left) and current system status (right)

The linear motion systems and basic components should be easily integrated into the control system, however, the integration of the printhead with the motion controller has proven difficult. The issue is that the printhead communication protocol is not compatible with just any control module. Team member Bill Carter has acquired a new control system that should be compatible with the printhead and will focus on that initially.

As far as the hardware is concerned, some of the custom-designed systems may require significant testing and redesign. One system in particular that could pose a major challenge is the powder dispensing and recovery system. This system was specially designed to both dispense and collect powder to and from the build volume and is the first of its kind. The powder recovery works by utilizing a vacuum to pull powder from the powder bed, and a cyclonic attachment to the top of the powder hopper slows the velocity of the powder down in order to be collected. The cyclonic action has not been testing and my need tuning and modification to work. Namely, a damping valve my need to be added to the vacuum line to reduce the air velocity, and a HEPA filter may be needed to eliminate powder from being pushed out of the hopper. If the mechanism overall does not work, the powder for this work will just be collected in a vacuum and not recycled into the hopper. Further, the dispensing plate that dispensing powder onto the layer may need to be redesigned as preliminary testing showed lack of fine control. Redesign of the system would include modifying the vibration mechanisms to have adjustability.

Other systems modifications and testing that will need to be completed include those related to the fluid systems. The printhead requires a supply of binder and cleaner, and the printhead cleaning station requires cleaning fluid. These systems will be supplied using peristaltic pumps that are activated when fluid reserves

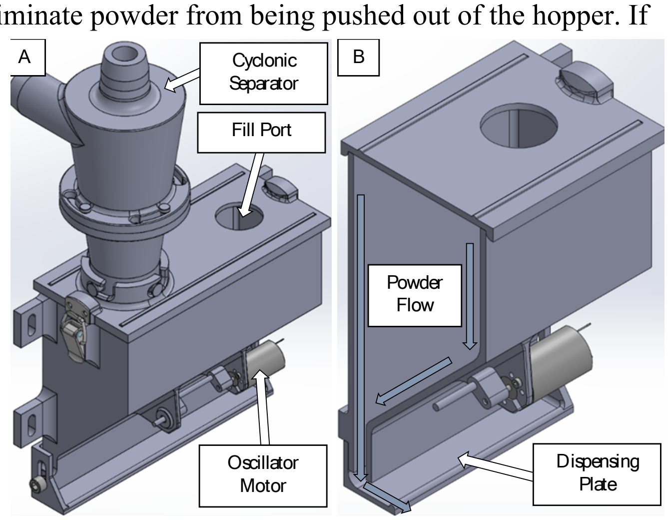


Figure 4. Hopper with cyclonic separator and oscillator motor (A); hopper cutaway showing the dispensing plate and powder flow represented by blue arrows (B).

are low, or the cleaning routine is activated. The fluid system itself will need considerable effort in tuning the parameters and timings.
Ultimately, the system suffered from challenges in communication between the main control system and the printhead. Multiple vendors were contact with no solution. The system was abandoned, and future research in this area will start with demonstration of the uses of multiple materials printed with binder jet followed by a new system construction.

Task 6: Polymers for filling and coating printed sand

One of the uses of binder jetting that is gaining popularity is the printing of sand molds for composite layups. The unique part of binder jet sand molds is that they can be washed away after molding, allowing for the layup of complex geometries such as exhaust manifolds for aircraft. The current limit to washout technology is need to seal/separate the sand from the epoxies used in the layup process so that sand does not become bound to the final part. The state of the art prior to this work was to wrap the printed sand parts in Teflon tape, which was labor intensive and not conducive for highly complex geometries. This task thus focused on a water-soluble, sprayable barrier coating that replaced the use of manual taping.

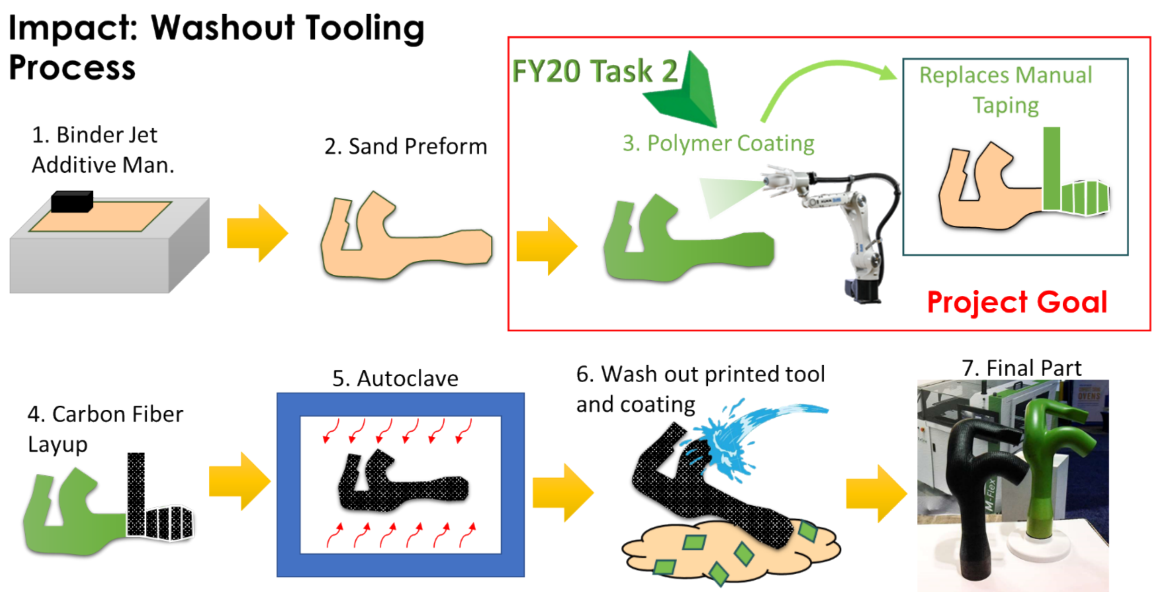


Figure 5: Illustration of project goal and washout process

The development of coating systems met many challenges including compatibility with the commercial sprayer, compatibility with the binder-jet binder system, over-penetration into the printed sand part, and compatibility with the layup materials and processing temperatures. Overall, a polymer system was developed and demonstrated as a viable candidate for layup coatings.

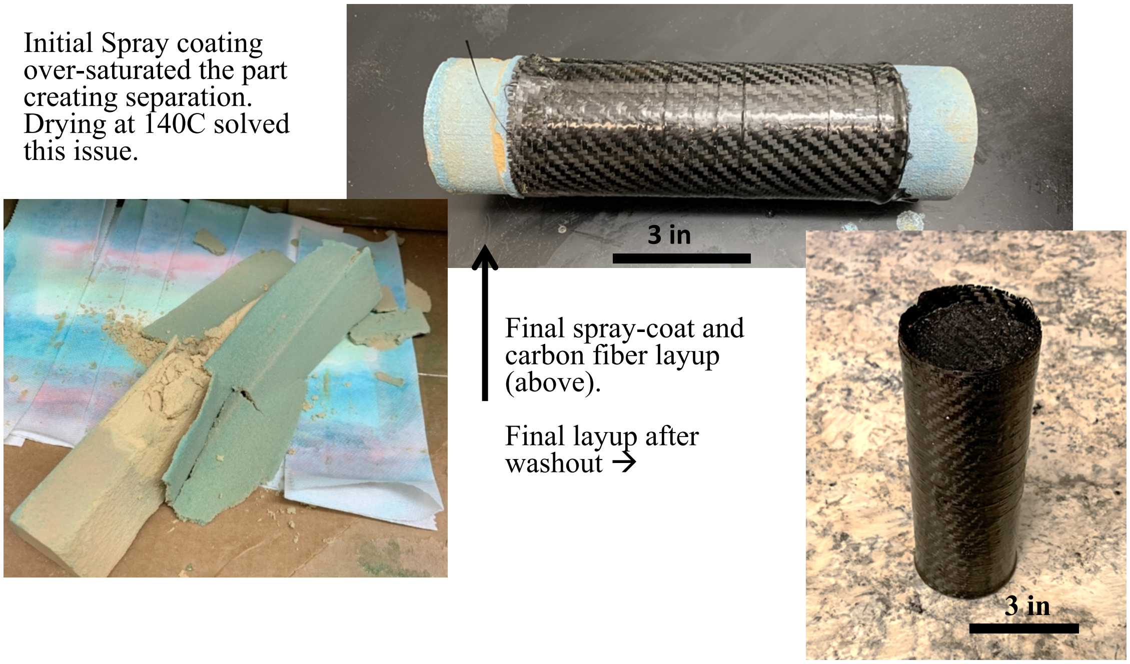


Figure 6: Experiments and results from layup coating development.

SUBJECT INVENTIONS (AS DEFINED IN THE CRADA)

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COMMERCIALIZATION POSSIBILITIES

Multiple patents have been licensed by the industry partner, including a technology not outlined in this CRADA but enabled as a by-product.

PLANS FOR FUTURE COLLABORATION

ExOne was recently bought by Desktop Metal, and the two companies are currently working to transition. It is anticipated that a new CRADA will be written for a collaboration with Desktop Metal in 2023.

CONCLUSIONS

The work performed during this CRADA resulted in multiple inventions and has improved the usability of binder jetting for various industries including composite tooling and MIM-replacement parts.

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