Polymer Spray Deposition: A Novel Aerosol-Based, Electrostatic Digital Deposition System for Additive Manufacturing

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Abstract

In order to address some of the shortcomings from traditional additive manufacturing methods, PARC, a Xerox Company, is developing a new additive manufacturing method for polymers that uses electrostatic patterning in combination with a new method of creating aerosols to directly pattern a wide range of thermoplastics with high resolution. Our aerosol technology takes advantage of the non-Newtonian nature of polymers to create monodisperse small droplets. In addition, we leverage ionographic printing techniques to pattern thick substrates and create digital thin films. This technology can bring 3D printing of polymers into a performance range where the technology can be used to replace more traditional techniques such as injection molding and machining.

Background

Additive manufacturing or 3D printing has been gaining interest as of late. It has the potential to revolutionize manufacturing around the world, giving manufacturers the ability to customize products for consumers, produce parts on demand, and even produce products right at the point of sale. However, while 3D printing gives producers the ability to create digital objects, there are often unacceptable compromises in part performance that come with 3D printing.

We can divide 3D printing of polymers into two main classes based on their input material. On one side, we have printing methods using curable materials. These processes include methods based primarily on photopolymerization such as stereolithography (SLA) or inkjet based printing approaches. On the other side, there are a range of processes that use forms of more traditional thermoplastics such as selective laser sintering (SLS) or fused deposition modeling (FDM).

Techniques based on photopolymerization are capable of an extremely high degree of fidelity and resolution. Common stereolithography techniques can achieve resolutions of tens of microns and using two photon polymerization even higher resolutions are possible. Inkjet based printers are capable of high speed and can print multiple materials simultaneously, enabling whole new ways of thinking about making things. However, these techniques use materials whose long term performance and stability is lacking. This lack of performance and durability has limited the use of these processes for the production of durable goods. While they have been used for the production of tooling, there are few demonstrations of these processes being used to print durable goods directly.

Thermoplastics are an ideal material to match the required performance of durable goods. These materials are commonly used to produce a wide range of objects. Injection molding is widespread and produces parts in almost every industry. There are numerous 3D printing processes that attempt to use these materials as a primary build material. FDM processes thermoplastics through a nozzle and can make objects from many thermoplastics. However, due to the raster style printing, and the relatively large size of the nozzle required these objects have a high degree of anisotropy and often have very low fidelity. SLS offers increases in both the consistency and resolution, but still cannot match the fidelity and resolution of techniques using photopolymers. In addition, the need to create a powder and limitations on the melting behavior of the material increase material costs.

Thermoplastic based processes cannot match the resolution and fidelity of photopolymer based processes because of inherent material properties of these large molecule materials. Polymers are high viscosity, non-Newtonian, and require processing at high temperature. This makes them difficult to process and incompatible with many high resolution processes such as inkjet.

An ideal polymer based 3D printer will be able to create objects from a wide range of thermoplastics at the resolution and fidelity of photopolymer based systems. Better yet, such a system would use the same feedstock as traditional injection molding to allow them to fully integrate into a manufacturing line.

Polymer Spray Deposition (PSD)

Polymer Spray Deposition (PSD), as shown in Figure 1, is a new method of additive manufacturing that has the resolution of photopolymer based system using thermoplastics as an input. In addition, this system uses the same thermoplastics, with the same form factor as injection molding to create a seamless digital system to replicate the performance of injection molding parts. This system will enable large scale digital production of durable goods.

In order to achieve this printing process, several important steps are involved. First, a high quality aerosol is generated using a newly developed spray technology called Filament Extension Atomization (FEA). A substrate is then charged through a combination of scorotron blanket charging and selective neutralization with ionographic printing. As the aerosol created by FEA is carried downstream to the printing surface, it is charged and exposed to the digitally patterned oppositely charged substrate. Being oppositely charged, the droplets are attracted to the still charged areas of the substrate, creating a digital film. Afterwards, any remaining charge is neutralized, the layer solidifies, and a support material fills in the rest of the print area, creating a new surface for the next layer.

This process can be completed layer by layer, resulting in a digital, high resolution object, made from high performance thermoplastics.

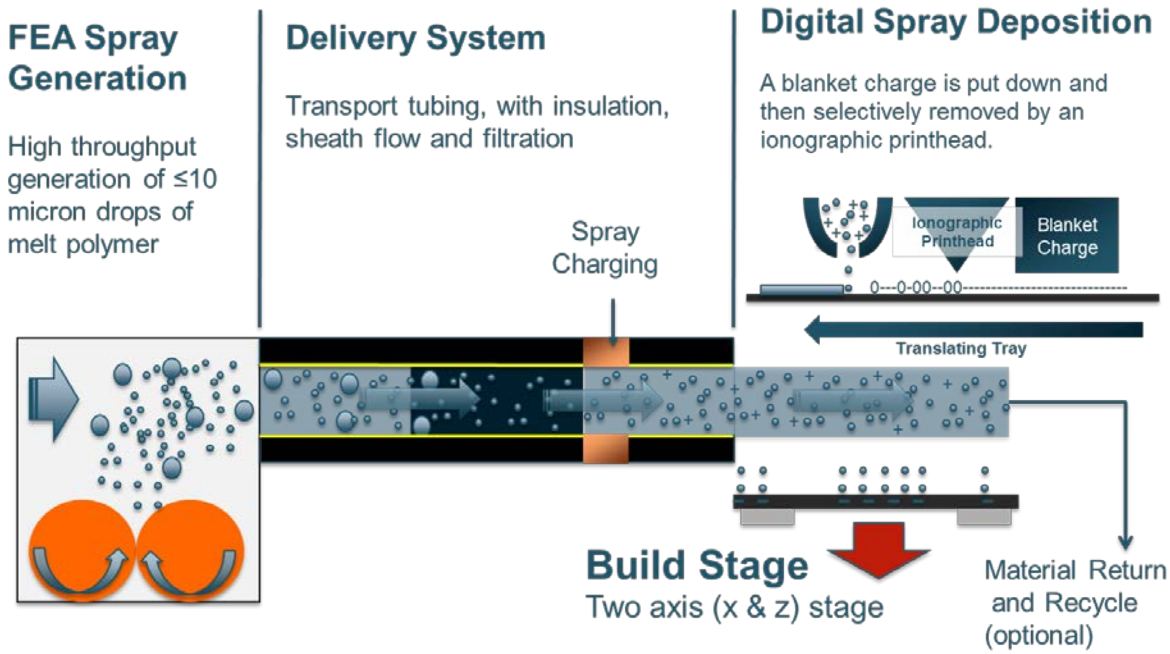

Figure 1 Polymer Spray Deposition process steps. From left to right, an aerosol is first produced using Filament Extension Atomization (FEA), it's then delivered to the target substrate and charged, the spray is then digital deposited onto the substrate. Digital patterning is achieved through blanket charging and then selective charge neutralization through ionographic printing.

Filament Extension Atomization (FEA)

Fluid atomization is a critical component of a number of manufacturing and industrial processes. The main purpose of such processes is generally to create a fine vapor mist or aerosol. Once a component, regardless of its properties, is made into an aerosol it can usually be readily processed to create a thin film or coating.

When the solution behaves like a Newtonian fluid, the creation of an aerosol can be accomplished via a number of traditional routes. The most pervasive of these is the use high momentum air flows to entrain air and liquid. A typical atomizer will involve the coaxial flow of air and solution. These flows are generally unstable and lead to fluid break-up via Rayleigh-Taylor and Plateau-Rayleigh instabilities. In many instances the flow is turbulent and chaotic, stripping and stretching fluid parcels at high strain and strain rates and thus leading to the entrainment of large amounts of air with the fluid. The result is a fine mist of drops suspended in air.

High velocity coaxial flows are very effective when the solution behaves like a Newtonian fluid, but many industrially important solutions, including thermoplastics, can contain a variety of macromolecular and interacting solid components. These components often lead to non-Newtonian properties, including shear-thinning and viscoelasticity. The non-

Newtonian properties can render atomization via traditional methods completely ineffective. For example, if a fluid is viscoelastic and strongly extensionally thickening, its extensional viscosity can increase by several orders of magnitude in the straining direction. [1] During jetting, this thickening causes the viscous drag to overwhelm the inertial and surface tensions forces, allowing the system to support large strain before breaking-up and preventing the formation of small drops. Instead, the jetting leads to the formation of long, sticky filaments, films and tendrils that fail to become suspended in air.

A principal problem with using coaxial flow systems to create aerosols is that the straining direction is coincident with the translation direction. The filament will eventually break-up, but to achieve the large strain the filaments issuing from the jet must necessarily travel long distances. As they travel, the filaments will lose momentum and can recoil to reform large drops. Alternatively, attempts to continually impel the filament during its trajectory are abortive as they would require impractically long jetting apparatuses.

As a filament relaxes, the formation of the beads-on-a-string structure occurs. These beads range in volume from pL to μL and serve as the precursors for the drops that will form at break-up. Since the drops are small volume, they will become suspended in air. This behavior can form the basis for creating small droplets from even exceptionally difficult to spray materials.

Breaking a single filament will not produce enough liquid volume to create a practically usable aerosol. Furthermore, it can be difficult to move a single surface up and down fast enough to create multiple filaments in a serial manner. In order to create and break multiple filaments rapidly, FEA technology uses two rollers with a thin film.

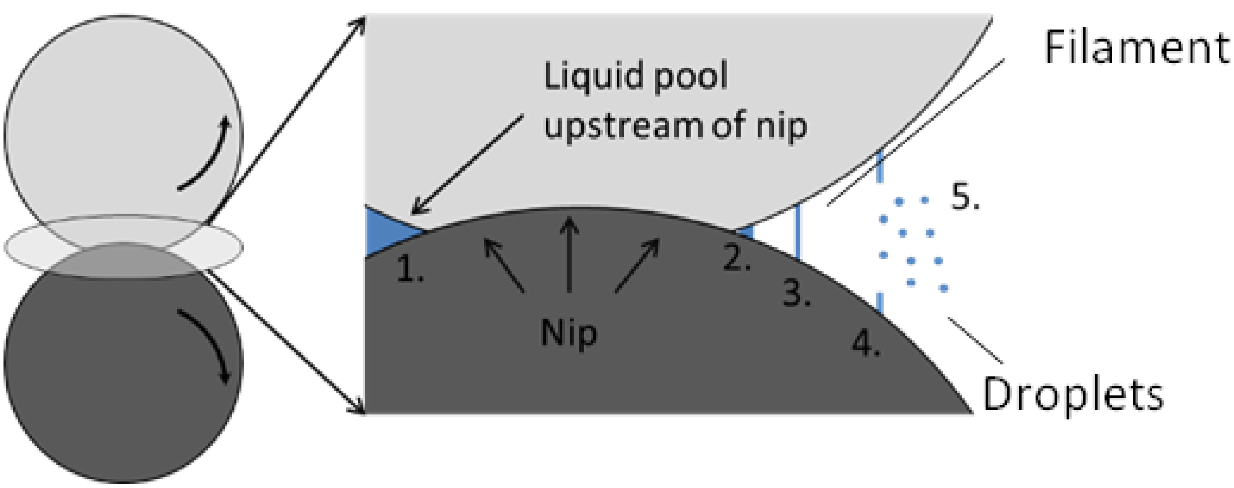

Figure 2 Basic steps in FEA spray technology.

FEA technology at its core consists of 5 main steps, as detailed in Figure 2. First, a liquid material (1) is taken into a tight nip, or contact area between two moving rollers. Downstream of this nip, the liquid is stretched between two rollers (2) where they eventually form discreet filaments (3). As the rollers continue to spin, they stretch these filaments to the point where they finally break into droplets (4). The droplets can then be harvested (5) and collected for further downstream processing.

In order to test this technology, PARC has developed a complete system to study droplets at both room temperature and at temperatures consistent with those necessary to process thermoplastics in liquid form. The room-temperature system provides valuable insight into the processing parameters required to spray materials, while the high temperature system provides confirmation of the performance of more useful thermoplastic materials. PARC has also developed a qualitative, high temperature version of an extensional rheometer. This system is capable of operation of up to 600°C and provides valuable insight into the extensional hardening behavior of materials.

Figure 3 PARCs infrastructure for studying spray and extensional rheology. Left a complete spray system for experimental work and right an extensional rheology device mounted inside of an oven.

Test material mixtures of 36% glycerol, 0.2% 5 million molecular weight polyethylene oxide, and water were used as room temperature solutions for testing of this system. To confirm the extensional behavior of the material, it was placed in the custom built extensional system and pulled 25mm at a rate of 50 mm/s. As shown in the screenshot in Figure 4 from video taken during the pull, the material clearly formed a filament, which started to break into droplets.

Two counter rotating rollers were used in the system shown in Figure 4 to test high output spraying. One was made from aluminum the other was composed of a shore 60A polyurethane coating. In addition, a feed system consisting of a syringe pump and doctor blade were used to create an even flow of fluid feeding into the nip.

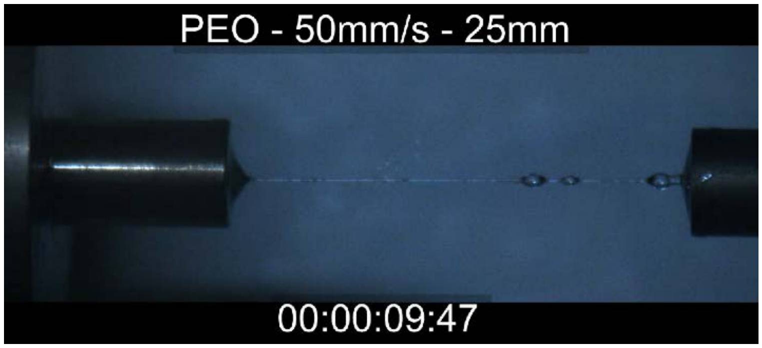

Figure 4 Filament breakup behavior of water, 0.2% polyethylene oxide, and 26% glycerol stretched between two pistons. The material can be observed forming filaments and forming small beads on a string.

This fluid was sprayed using both the PARC FEA spray system and a high pressure paint sprayer (Graco Magnum ProX9) running at 207 bar. Using this high pressure spray washer, a droplet size distribution was obtained using a Malvern Spraytec laser diffraction system. Drop size distributions, detailed in Figure 5 were obtained. Although some small droplets were obtained from the pneumatic paint sprayer, a large number of large droplets were also obtained. In addition, as shown in the screenshot from high speed video, the quality of the spray was low with a large number of filaments in the aerosol. In contrast, FEA technology was able to produce nearly monodisperse droplets below 1 micron in size. These droplets were spherical and tightly distributed.

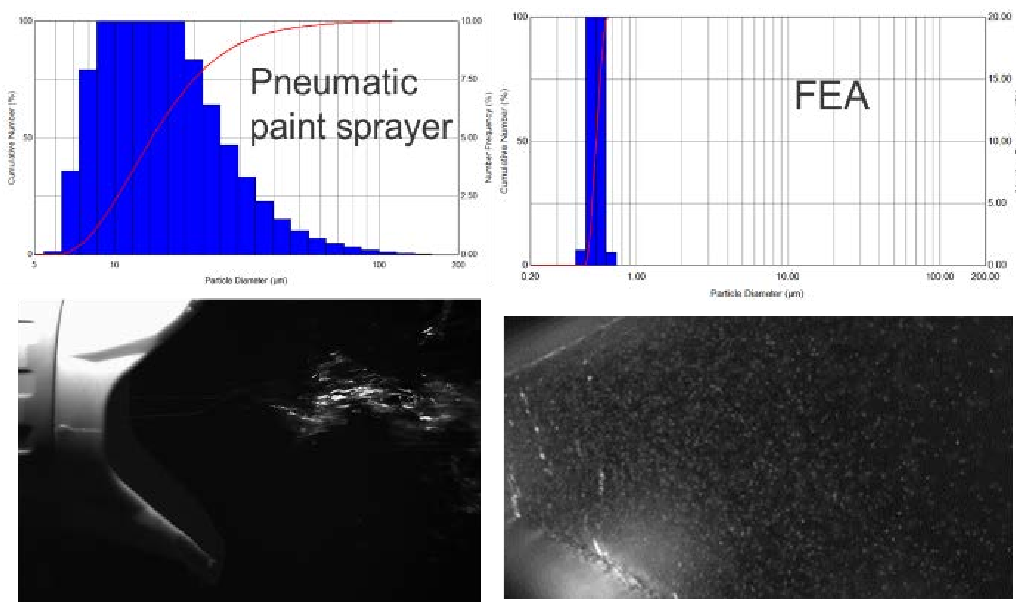

Figure 5 Comparison of drop sizes produced from FEA technology (right) and a pneumatic paint sprayer (left). FEA produces small, spherical, monodisperse droplets that are ideal for high resolution processing.

This technology is also readily applicable to polymer melts as well. Pro-fax PD702 manufactured by Lyondell Basell was chosen as a first test material because it is a commonly used injection molding material. In order to test the spray performance of this material, it was tested in both PARC's single filament and roller based systems. At a temperature of 230□C, PD702 was pulled 10mm at a speed of 0.2 mm/s. The material was observed to create a filament and beads on a string that would result in droplets to be harvested as spray.

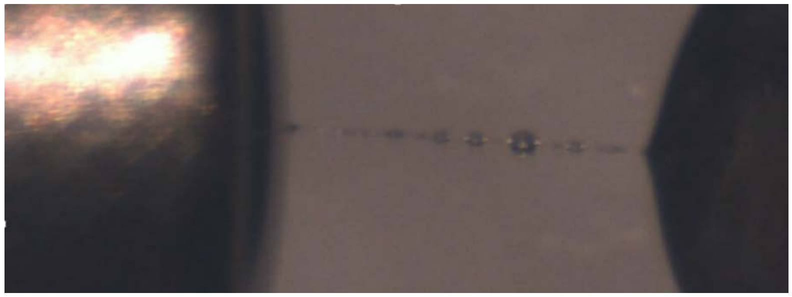

Figure 6 Polypropylene filament formation and droplet breakup behavior.

The material was then loaded into a high temperature FEA system and sprayed. As shown in the screenshot from high speed video, the material forms filaments, which break into droplets for further downstream processes. A glass slide was placed in front of the rollers where the droplets were impacted on the slide. Droplets were imaged using a Keyence VHX-5000 after they had cooled. These droplets can be produced at a wide range of sizes to fit the needs of downstream processing steps.

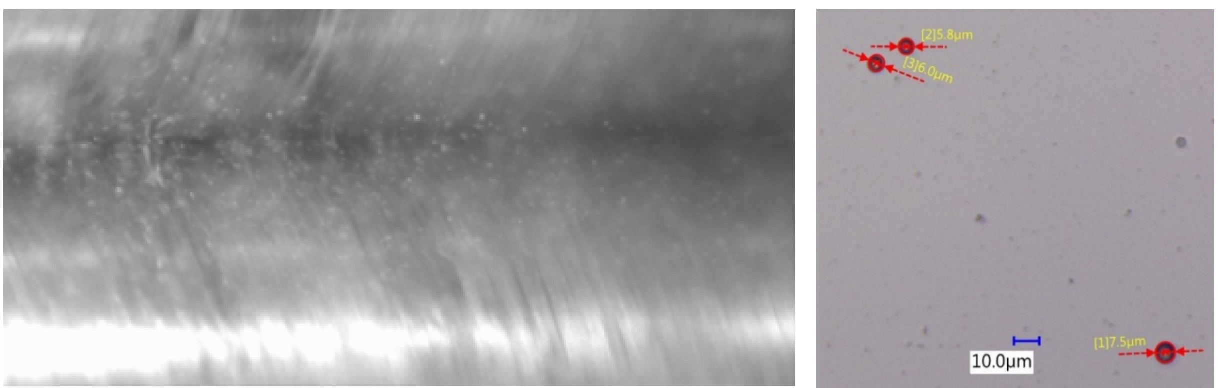

Figure 7 Screenshot from high speed video of polypropylene being sprayed. Filaments form and breakup into droplets successfully. The droplets were collected on a glass slide and the impacted diameters measured using a Keyence VHX-5000 digital microscope.

With a feedstock of thermoplastic material, the possibility of digital printing thermoplastic material with high resolution printing methods is possible. Furthermore, additional testing of the FEA system has shown that droplet size can be manipulated, allowing it to be adapted to the needs of the printing system.

Ionographic Based Digital Substrate Charging

Electrostatic charging systems are commonly used in printing devices. Over the years these have taken various forms, including electrophotography and ionography. In two dimensional printing, these methods have proven to be high quality, high resolution, and low cost methods to produce digital images. However, electrostatic methods of additive manufacturing have yet to take off.

In Polymer Spray Deposition, a 5 step printing process is used to deposit aerosol material. Steps 1-3, the digital imaging and deposition processes, occur serially as either the substrate or the printing heads are moved across the substrate in a single axis. Finally, steps 4-5 occur as blanket steps to neutralize any remaining charge and fill the negative space in with support material to create a blank surface for the next layer. By repeating these steps and moving the substrate relative to the printheads in a direction normal to the print plane, a 3D object can be created.

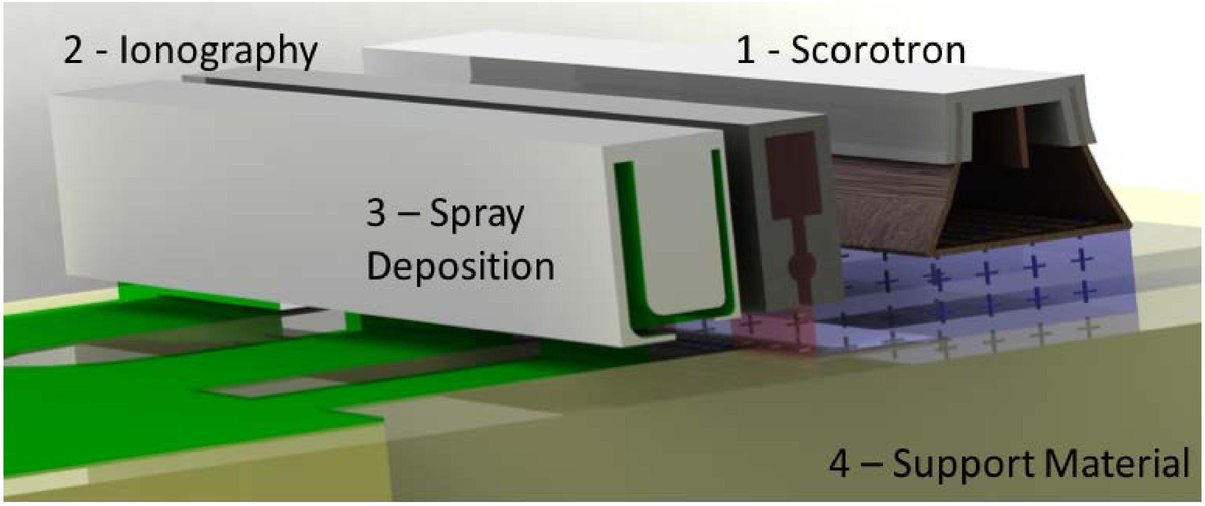

Figure 8 Digital patterning steps in PSD. (1) a scorotron is used to deposit a blanket charge, (2) the charge is selectively removed with an air assisted ionographic printhead, and (3) oppositely charged spray is deposited

Each layer print process starts with a uniform flat surface covering the entire print area. This means that support material must be filled in around the entire object. To be able to deposit a uniform charge, a scorotron is used to charge the surface up to one potential, in this case positive. A scorotron is ideal for charging this surface, since ions can accelerate towards the substrate due to the differential potentials of the screen and the ion source.

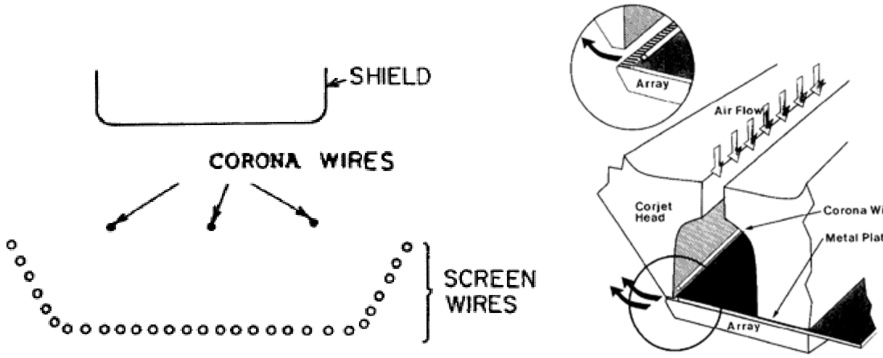

Figure 9 (LEFT) Basic layout of a scorotron charging device. [2] and (RIGHT) Cross section of a Corjet printhead, developed by the Xerox Corporation. [3]

After blanket charging the surface, an ionographic printhead is used to selectively remove charge from the surface. In this case, the ionographic printhead removes charges from areas where printed material is not desired.

Iongraphic printing techniques work by controlling the projection of ions onto a substrate in order to create a digital image that can be developed with either a solid or liquid toner. Several different implementations of ionographic printheads have been developed. Corjet, a Xerox developed ionographic printhead, utilizes a pressurized airstream to carry the ions towards the surface.[3-7] This air stream is important in order to print on this substrate since the ground plane is far away and hence cannot be relied upon to accelerate ions towards the surface.

Corejet based ionographic printhead, turns pixels on and off by modulating electrodes placed near the exit. When these electrodes are turned on, they attract and neutralize the charged ions. This printhead architecture is relatively simple, which allows the construction of this printhead from a wide range of materials, allowing for process air to be well above room temperature. This process air can be used to ensure the substrate surface is at the right temperature in order to assure maximum adhesion of droplets to the surface.

Once a digital electrostatic charge is achieved, a stream of oppositely charged aerosol, produced with FEA technology, is passed within close proximity of the substrate. This oppositely charged aerosol is attracted to areas where charge has not been ionographically removed. A single digital layer of droplets has now been deposited. Droplets are kept at elevated temperature, ideally near the same process temperature they are processed through FEA, in order to ensure excellent adhesion to the previous layer. These droplets will eventually cool and forma cohesive structure with prior layers.

Following the deposition step, a charge neutralization step occurs in order to minimize any charge build up and then a support material is filled in to create a geometrically uniform surface for the next printing step. The process is repeated as necessary to produce a digital 3D object.

Summary

Polymer Spray Deposition (PSD) has the potential to be a powerful tool for 3D or 2D printing applications. FEA technology allows thermoplastic polymers, which previously have been challenging to process at high resolution digitally, to be sprayed into an aerosol, which can be processed using high resolution, high speed and high resolution, electrostatic techniques. This will enable the production of high resolution objects from a wide range of conventional thermoplastic materials. Instead of having to develop separate materials for 3D printing, the same materials commonly used in injection molding can be used. This will enable 3D printing and additive manufacturing to change from a technique primarily good for look and feel, to a technique entirely suitable for test and use.

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Author Biography

Founded in 1970 as Xerox PARC, Palo Alto Research Center was incorporated in 2002 as an independent, wholly owned subsidiary of Xerox Corporation (XRX) today known as "PARC, a Xerox company" or just "PARC". PARC has been instrumental in the development of a wide range of printing technologies including laser printing, inkjet, ionographic printing, digital paper, and printed electronics. Additionally, PARC was instrumental in the personal computing revolution, helping to launch technologies such as the graphical user interface, and ethernet. Today PARC practices open innovation with clients around the world. Through multidisciplinary competencies, PARC advances technologies in printing, novel electronics, clean tech, advanced manufacturing, networking, intelligent systems, and ethonography with multi-disciplinary teams.

David M. Johnson holds a BS in Mechanical Engineering from Cornell University and leads the Advanced Manufacturing and Deposition Systems group within the Hardware Systems Laboratory at PARC. The group's main focus is on platform technologies with the ability to impact a broad range of industries. We strive to develop systems that increase overall system level performance without necessarily requiring advancements in material performance. This is accomplished through even greater control over the manufacturing process and often increased digital fidelity, all while striving to ensure our systems are readily scalable from conception