Additive Manufacturing by Electrophotography: Challenges and Successes

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Abstract

3-D printing of complex structures by selective deposition is currently dominated by direct write and inkjet technologies (as utilized in Stratasys, Objet, ZCorp, Voxeljet, and Solidscape systems). Dry toner systems, despite their high productivity and maturity in 2D digital printing, have only been used indirectly for Additive Manufacture (AM) of objects above the micro scale. For over 3 years a European consortium has sought to overcome the inherent challenges of multilayer printing by electrophotography to enable its use in mainstream AM which promises increased deposition efficiency and a means of utilizing materials not amenable to liquid ink formulations. This paper reviews the challenges addressed and demonstrates the progress made including development of a bespoke thermoplastic elastomer toner and the specialized hardware configuration used to print and fuse it into tensile specimens over 50 layers thick which elongated over 500% before failure. Additionally, seeking to reduce oxidation during toner fusing, electrostatic printing and fusing was unsuccessfully attempted in a vacuum and in argon; while printing in a partial vacuum (above 50 kPa) and nitrogen was possible.

Introduction

From the 1970's electrophotography has continually pushed digital printing techniques to higher standards of speed, resolution, and reliability. Despite the proven capabilities of dry toner printing, its contribution to the emergence and development of 3-D printing or additive manufacturing (AM) systems during the first twenty years has been conspicuously absent.[1]

AM is a digital fabrication process which usually forms material into layers and joins multiple stacked layers together to create three-dimensional objects. To date the commercial implementation of electrophotography in AM has been confined to the generation of temporary masks for selective exposure to ultra-violet and infrared radiation by Cubital (Israel) and Sintermask GmbH (Lupburg, Germany) respectively.[2] The direct deposition of dry powder to form layers for the creation of 3-D objects has received attention from a variety of researchers with some success at the micro scale.[3-8] However, these attempts still fail to deliver objects on the same scale as mainstream AM techniques which utilize methods including direct writing (FDM, syringe deposition), inkjet (3DP, Polyjet, Voxeljet, Wax jetting), and laser based approaches (SLA & LS).[9]

Progress toward fully implementing electrophotography in AM is reported. The research centered on a bespoke AM system based on two component printing of non-magnetic toner and infra-red fusing. The hardware configuration, toner materials, and testing of the multilayer samples produced as well as the feasibility of electrophotography in inert environments are discussed.

Equipment

To enable multi-layer printing of non-standard toner materials a test rig was built using twin CTG-1C17-600 printers (CTG PrintTEC, Germany). Two printers were used to enable printing of two different materials. Usually the first printer was loaded with the toner to be fused into the final component and the second printer with a temporary material for supporting overhanging features which can be easily removed after the printing process. The printers were mounted onto a machine frame above a 2-axis motion system (6 m x 500 mm stroke) which enabled printing onto a moving flat build platform (500 x 500 mm) as shown in Figure 1.

Printing Process

The printing process comprises the following steps: a. A print was sent to (one or) both printers b. the platform traversed along its horizontal axis synchronizing its speed with the surface of the final transfer rollers c. The images were transferred onto the platform d. The platform was driven underneath a medium wave 12 kW infrared heater (Infra-red Systems, England) to fuse the newly deposited toner e. The platform dropped by the thickness of the layer just printed f. The cycle was repeated for each additional layer required. The process is called Selective Laser Printing (SLP).

Figure 1 *- Selective Laser Printing (SLP) Development Rig*

Optimizing Mechanical Properties of Toner

Perhaps the most drastic difference between the requirements for AM versus printing on paper is the mechanical properties of the toner. Many conventional toners for printing text and images are based on brittle polymers with low melting points, which readily tribocharge, such as: styrene, acrylics and PVA. Their brittleness facilitates particle reduction by mechanical (air jet) milling and also imparts scratch-resistance once fused into text and images on paper. A low melting point is also desirable to enable

rapid fusing. In contrast to the needs of conventional toner, service conditions of AM parts could include relatively high forces and temperatures, with a preference for tough materials with a propensity for elongation rather than cracking.

The shortcomings of using conventional toner for AM have been demonstrated by researchers who attempted to build up thickness by multiple prints of standard black magnetic toner supplied and printed with a Laserjet 4 printer (Hewlett-Packard, USA). The samples produced were "extremely fragile" and crack formation was evident on the surface after only 10 printed layers.[7]

Development of new toner materials

The development of new toner materials based on engineering polymers seems an obvious next step, however the selection is governed by the need to produce (or reduce) the powder to an appropriate particle size range, and selecting materials which will tribocharge favorably for the photoconductor of the intended printer. Furthermore, many applications demand a pure or nearly pure material after deposition which restricts the formulation to non-magnetic toners. To date, researchers have demonstrated the possibility of printing toners formulated predominately from: high and low density polyethylene, polypropylene, and water soluble polymers.

In order to circumvent some of the development time typically required for full-fledged new toner formulation, a surface coating technique implemented by Banerjee and Wimpenny was used.[7] Somos 201 (3D Systems, USA), a proprietary thermoplastic elastomer material formulated for laser sintering which exhibits properties similar to polybutylene terephtalate (PBT) was classified into a suitable particle range (nominally 35 µm) and surface coated with 0.5 Wt.% of fumed silica to improve its flow and charging characteristics. The new toner was mixed with a suitable carrier in a 10 Wt.% concentration and loaded into the developer unit. Tensile test specimens were printed using the SLP development rig as shown in Figure 2. Each newly deposited powder layer was heated to the Tg of Somos 201 (115° C which was determined experimentally) and contributed approximately 11 to 12 µm to the overall deposited height. Specimens averaged 0.78 ±0.017mm high.

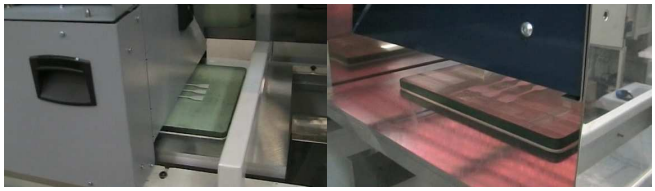

Figure 2 *- Selective Laser Printing – Printing and Fusing*

After the specimens cooled they were peeled off the platform and examined by SEM and tensile testing. Attempts to obtain a fractured surface through the cross-section of one specimen for SEM by submerging in liquid nitrogen and bending failed to result in a clean break; therefore a cross-sectional cut was made. The micrograph (Figure 3) shows a very high degree of particle coalescence throughout the cross-section except at the uppermost surface of the specimen (where the layers have been most recently deposited).

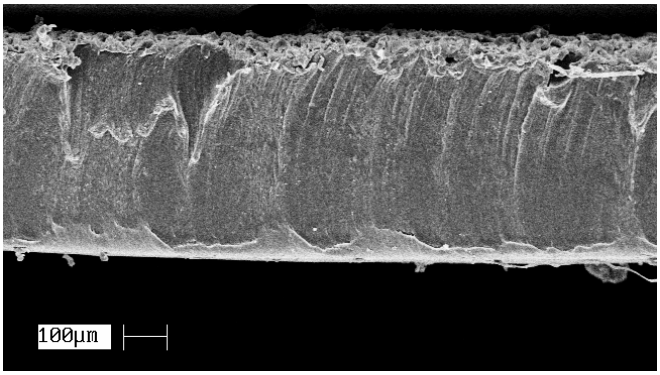

Figure 3 *– Micrograph of the cross-section of a specimen produced by SLP*

Tensile testing was carried out on an M250-2.5kN (Testometric, England) with a cross-head speed of 50mm/min at 19°C and 40% RH. Tensile testing of the set of specimens as shown in Figure 4 demonstrated an average elongation of 205 ± 14.2 mm from a 40 mm original gauge length giving an average elongation at failure of 513 ± 35%. These results are on the same order of magnitude as parts created by conventional injection molding.

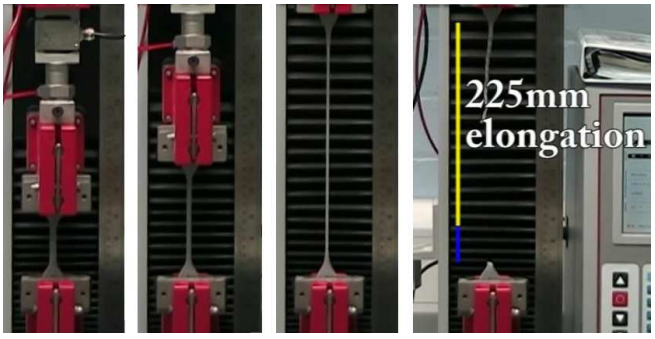

Figure 4 *– Tensile test of specimen produced by SLP*

The potential for electrostatically printing tough flexible polymers has been demonstrated. The cohesion of toner particles into a single body with simple geometry with near full density has been shown by SEM. The characteristics of the resulting part have also been indicated by tensile testing. This work forms the foundation upon which full-fledged toner based on engineering polymers could be based. Future work could address issues including toner efficiency, yield, background printing, and elimination of toner back transfer (some of which fused onto the photoreceptor).

Deposition in Inert Environments

In addition to developing new toner materials it is also crucial that they be fused under optimum conditions. It is common practice in thermally based AM processes such as laser sintering and electron beam melting to fuse powder in an inert environment

which improves material properties by minimizing oxidation (as in Arcam, EOS GmBh, 3D Systems and MTT Technologies systems). Following this pattern, the viability of electrophotographic printing in inert environments came into question. In response, the deposition density of a LaserJet 1200 (Hewlett-Packard, USA) was tested using standard black toner (C7115X, Hewlett-Packard, USA) printing the ASTM F 2036 - $05^{\epsilon 1}$ test pattern on 80 gram paper in a 5/05 vacuum chamber (MCP, Germany) at various levels of vacuum and relative humidity with and without inert gas backfill as summarized in the subsequent tables. The vacuum pump was switched off when each target pressure and relative humidity was reached and the print sent within one minute. Between each set of trials the vacuum chamber was vented, the door opened, and purge prints were made until the print density returned to normal. Throughout the trials, the temperature and humidity inside the chamber was measured with a 408-6109 hygrometer (RS Components, England) and verified with a 971 Temperature Humidity Meter (Fluke, USA) before and after depressurization. Throughout the trials the ambient temperature varied between 21.4 and 23.9°C and relative humidity between 37 and 41%. Due to the fact that the operational range of most printers is specified between 20 and 80% relative humidity, tests run outside that range (due to dehumidification induced by chamber depressurization at room temperature) were re-run after the relative humidity inside the chamber had been raised to within that range.[10]

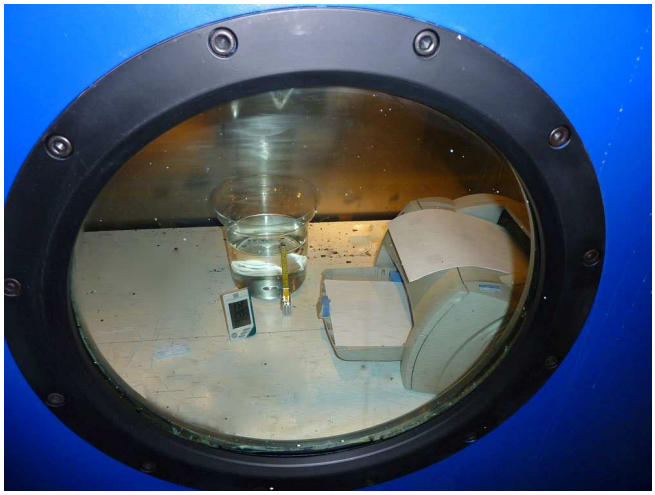

Figure 5 *– Printing in a vacuum chamber*

The resulting printed patterns were then evaluated according to ASTM F 596 where the rating scale used for comparison was the average percent brightness in the printed areas. This was determined by scanning the print patterns at identical settings (16-bit grayscale, no color correction) and then the brightness in the printed areas was averaged using software to give an average brightness value from 0 to 100% (where 0 = black and 100 = white) as an indication of print density (Figure 6).[11] This software averaging evaluation method was selected as the most robust indicator across the unusual variety of deposition density and fill patterns (Figure 8).

Test Matrix: Print density in decreasing pressure

Pressure	RH <20%	20-29%	30-39%	40-49%
101.3 kPa				■
84.4 kPa			■	
67.4 kPa			■	
50.5 kPa		■		
33.6 kPa		■		□
2.4 kPa	■	□		□

■ = No added humidity □ = Re-run at higher relative humidity

The results of printing in the vacuum chamber without increasing the humidity in the air are shown in Figure 6. The upper portion of the figure shows the test patterns as printed in decreasing pressure and the lower portion shows the average percent brightness. Prints at 101.3 kPa (1 atmosphere) were made with the chamber door open and averaged 8.2 ± 0.37% brightness. There was clear correlation between the diminished density of the printed images and the pressure drop. Prints at 84.4 and 67.4 kPa were nearly as dense as those at 101.3 kPa with 10 ± 0.31% and 10.4 ± 0.24% brightness respectively, although print defects were more evident as pressure decreased (see the 67.4 kPa print in Figure 6). Prints at 50.5 kPa dropped considerably in density to 15.76 ± 0.67% and there was no image deposition at or below 33.6 kPa.

Owing to the fact that depressurization also dehumidifies, the reduction in print density also correlated with reduced relative humidity (RH). In order to isolate whether the primary factor inhibiting print density was lower pressure or RH in the chamber, prints at 33.6 kPa and 2.4 kPa were re-run with an open container of water inside the chamber (Figure 5). When the chamber was pumped down to 2.4 kPa the water boiled. Once the RH reached the desired level the vacuum pump was turned off and the boiling would stop. If a higher pressure was required, more air (or an inert gas) was leaked back into the chamber, but only after the RH was inside an acceptable range. Prior to this experiment it was hypothesized that introducing water vapor into a nearly airless chamber might, in the presence of high voltage, disassociate and ionize sufficiently to act as a medium to allow printing however that was not the case. Even in the presence of increased humidity no toner was printed at the lower two pressures.

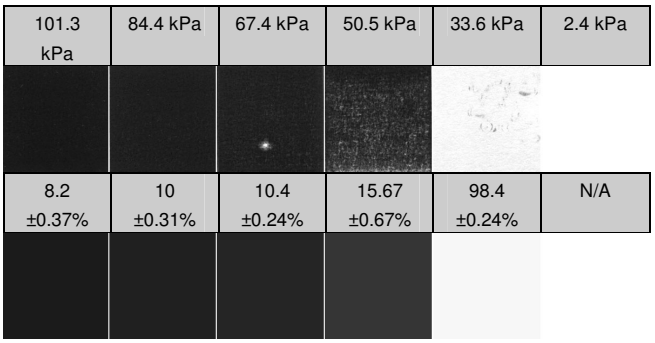

Figure 6 *– Print density in decreasing pressure. As printed (above) and averaged % brightness using software (below).*

Having established a lower pressure threshold below which printing is not viable the medium-term effects of printing in a

partial vacuum were explored. At a sustained pressure of 67.4 kPa a print was made after 2, 4, 8, and 16 minutes yielding an average brightness of 13.8 ± 1.59%, 9.6 ± 0.4%, 9.0 ± 0.32% and 8.6 ± 0.4% respectively. Excluding the first print, the print densities of the subsequent prints are clustered together and improve slightly with each print, indicating that the duration a printer is in a partial vacuum has no adverse cumulative effect on the print density over time and may even be slightly beneficial. It is surmised that extended durations in partial vacuum could reduce humidity held in the paper in the same way that heaters (or air-conditioning units) are used to moderate humidity in many printers.

In order to observe which components of the printer were most susceptible to depressurization a series of prints was done in decreasing pressure as per above, except that the print was halted mid-print to allow inspection of the photoreceptor (Figure 7). The pressures and RH values at which the image did not print correlated precisely with the results above (no deposition at or below 33.6 kPa) and in each case where there was no transfer onto paper; toner had not been developed onto the photoreceptor either.

Figure 7 *– Inspection of image development stopped mid-print*

The above result indicated that a gaseous medium, presumably needed as an ion source, is required to facilitate image development (and possibly transfer) in a LaserJet 1200. The next trial explored if other gases can be used as a substitute for air.

Test Matrix: Print density in inert gases

Gas	RH <20%	20-29%	30-39%	40-49%
Nitrogen	■		□	
Argon	■			

Nitrogen and argon were selected on the basis that they are the most commonly used inert/semi-inert gases for processing of materials in AM (EOS GmbH, 3D Systems, MTT Technologies Ltd). For each of the inert gases the chamber was depressurized to 2.4 kPa and backfilled to 101.3 kPa (1 atmosphere) with said gas. The nitrogen with low humidity printed almost as well as in ambient air (at 101.3 kPa) with an average brightness of 10.9 ± 0.46% and slightly less densely (12.2 ± 0.39%) at 30.5% RH (where the humidity in the chamber was increased as described above). This result was slightly surprising because normally electrons do not easily attach themselves to pure nitrogen, argon or helium gases so they do not form stable negative ions which generally occur in gases containing oxygen, carbon dioxide and water vapor.[12] Except for the first print no deposition was achieved in the argon. After the successful printing in nitrogen this result was also a surprise because the ionization potential of argon is so close to that of nitrogen (15.6 and 15.8 respectively).[13]

The initial print after arriving to each new pressure and RH varied from the subsequent prints carried out at those conditions. This was most evident when printing in argon at 101.3 kPa, and air at 2.4 kPa and 42% RH. In the first case a strange pattern was generated within the developed image area and in the latter the entire paper was printed with a non-uniform pattern (Figure 8). In both cases no image was generated on subsequent printing attempts. Presumably, these unusual initial prints were the result of ions retained in the printer due to residual charges generated during the purge prints which immediately preceded depressurization (and backfill) of the chamber for the trials. Whatever the reason, those circumstances did not persist after the initial print and subsequent attempts to print in those conditions came out of the printer blank.

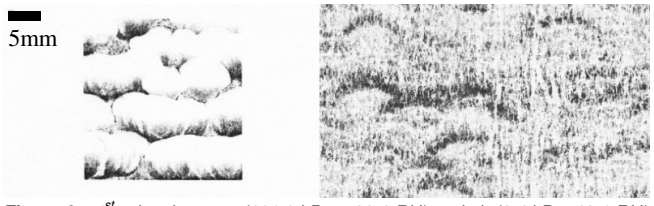

Figure 8 *– 1st prints in argon (101.3 kPa, <20% RH) and air (2.4 kPa, 42% RH)*

The behavior of a laser printer at and below 101.3 kPa (1 atmosphere) in a vacuum chamber has been demonstrated. The print density as indicated by average percent brightness (of printed areas) was reduced with depressurization and no electrophotographic development occurred at or below 33.6 kPa (below 41% RH). This showed that a gaseous medium is required to enable electrophotography. Of the two inert gases tested, argon severely inhibited print density while a nitrogen rich atmosphere was used with only minor impact. As a final observation it should be noted the paper feed mechanism was not intended to operate under vacuum which induced double, triple, and even quadruple page feeds frequently jamming the printer (although this phenomenon was observed less frequently when the humidity level was artificially raised inside the chamber).

Conclusions

The possibility of printing mechanically functional toners with over 500% elongation has been demonstrated. The feasibility of printing in a nitrogen atmosphere to allow optimal thermal fusing conditions has also been shown. Future work will expand upon the range of functional polymers that are formulated as fully fledged toner and quantify the benefits of fusing them in a nitrogen atmosphere. The emphasis of future printed samples will be on increasing deposition volume and height. Furthermore, there is a need to expand upon current 2-D evaluation techniques to enable them to characterize 3-D printed structures robustly.

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Author Biography

Jason Jones has undertaken research in the field of Additive Manufacturing since 2005. He joined the Innovation Centre at De Montfort University in 2007 as a Senior Research Fellow to lead collaborative research projects. He explores applications for customised products and develops new layer based manufacturing techniques by electrophotography and direct writing. He is also active on the ASTM international standards committee for Additive Manufacturing.

For five years prior to his current appointment, he worked in the CNC & 3D printing industry as Technical Manager for Unimatic Engineers in London, England.