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Simple sensor manufacturing by Laser Powder Bed Fusion of conductive polymer blends

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Abstract
The efficacy of manufacturing conductive plastic components by the Material Extrusion (MEX) method has been shown previously by Grønborg et al. [1]. To increase the effectiveness of additive manufacturing of these sensors a study utilising Polymer Laser Powder Bed Fusion (L-PBF) technique has been undertaken. The study investigates; the conductive networks created during manufacturing and the influence of processing parameters on the conductivity of the parts. The test specimen has been manufactured on the Open Architecture Polymer L-PBF system developed at the Technical University of Denmark. Utilising the capability of full-scale process control, and the implemented high-power fiber laser to achieve consolidation of the powder. The feedstock material has been designed to allow high energy absorption at the fiber laser wavelength (1080 nm), and thermal properties to comply with the L-PBF process. A conductive network manufactured by the Polymer L-PBF process is demonstrated. The parts produced have been tested by measuring the material's conductivity at the initial unaltered state, and further investigated by SEM micrographs to conclude on the stability of the manufactured parts.

1. Introduction

This work presents the current state of Additive Manufacturing (AM) of flexible polymer parts, which show conductivity, by Polymer Laser Powder Bed Fusion (PL-PBF). PL-PBF is a method of AM, processing powdered polymer into parts, by selectively sintering a geometry layer by layer using a mirror-guided laser beam [2]. Utilising the PL-PBF technology allows for building 3D parts without support structures or other unwanted attached geometries. The parts can be post-processed depending on the desired finish but can be used directly from production with minimum post-processing. PL-PBF can be used for direct manufacturing of wearable sensors, which fit perfectly for the individual, where a close fit will benefit the sensor's capabilities.

Athreya et al. (2009) [3], conducted a study on the manufacturing of conductive polymer parts from the PL-PBF process and successfully manufactured conductive parts made from a blend of PA12 and Carbon Black. Athreya et al. (2009) [3], investigated the effect of coating PA12 with a nanoparticle carbon black powder to produce a conductive PA12 part. The conductivity was for the case of PA12 coated by carbon black by five orders of magnitude. The study also concludes that no significant change in the crystalline morphology was observed.

The present research has been conducted as a proof-of-concept for consolidating a powdered flexible polymer blend composite into electrically conductive parts. A blend of a conductive polypropylene with a high loading of carbon black, and a flexible thermoplastic polyolefin elastomer, is developed for the study. The work consists of developing the polymer blend composite with consideration towards the PL-PBF process requirements, micronisation of the polymer pellets and qualifying this powder. As well as investigating the electrical conductivity of these parts. The study uses two different process parameter approaches for the production of parts, which will be used to conclude the influence of these process parameters, on the conductivity of the parts.

2. Materials and Methods

The experiments considered several factors for defining the efficacy of producing conductive parts by PL-PBF. The materials were developed and produced to align with the process capabilities of the Open AM machine. The production process was designed for the specific powder, with two separate process parameter sets developed. Furthermore, the electrical conductivity of the parts produced was tested to conclude the effect of process parameters.

2.1. The Open AM PL-PBF setup and parts produced

The conductive test specimen was manufactured on the Open Architecture PL-PBF system developed at the Technical University of Denmark [4]. The Open Architecture allows complete control of the processing parameters, including; scanning speed and strategy, as well as control of the chamber heating. The system uses a high-power fiber laser (1080nm), contradictory to an industrial system using a CO2 laser (10,6µm). The fiber laser allows for better laser tuning and a gaussian beam profile, with a high energy absorption into the black constituent of the powder [3,5]. The parts produced on the system were a 10mmx50mm rectangle, produced as a single layer. The single-layer approach was selected for the proof-of-concept for manufacturing consolidated parts, that show conductivity, from

a material designed for PL-PBF. The parts are produced in the atmosphere without saturation of inert gas.

2.2. Material development

A conductive polymer blend composite consisting of 60/40 wt% Cabelec CC6057 conductive concentrate from Cabot Corporation with a Conductive Carbon Black content of 40% (MFI 1g/10min 230°C/5kg), and Vistamaxx 6502 from ExxonMobil (MFI 45g/10min 230°C/2,16kg), respectively was compounded for the study. Cabelec CC6057 was chosen for its ease of handling and good electrical conductivity (~9,0*10^2 Ω/sq, according to the datasheet). Vistamaxx 6503 was selected for its flexibility and compatibility with the conductive concentrate. Both materials showed a promising thermal processing window for PL-PBF. The compounding of the conductive polymer blend composite was performed on a Thermo Fisher Eurolab 16XL Twin Screw Extruder with a set of medium shear mixing screws with an output of 2 kg/h at 75 RPM. The temperature profile of the extruder was, from the die: 200-200-200-200-200-200-200-170-130-80°C. The Cabelec 6057 was dried at 80°C in a hot air dryer for at least 12 hours ahead of processing. The extrudate was cooled in a water bath and subsequently pelletised and dried to remove any water from the cooling bath.

From the pelletized material, a powder was produced. The Powder was made by Cryogenic ball Milling using a Retsch CryoMill, running at -196°C with 2 minutes of cool-down time and 30-second intervals of grinding and cooling, respectively. The powder obtained was sieved, and the fraction below 96µm was used for part production. The powder was quantified by laser diffraction using the Malvern Panalytical Mastersizer 3000 with the dry cell attached.

2.3. Process development for SLS

An understanding of the processing capabilities of the powder is developed based on the DSC analysis of the conductive polymer material. The DSC scan was carried out at standard conditions in a nitrogen atmosphere, with a heating rate of 10.00°C/min from temperatures of -95°C to 230°C followed by a cooling down to -95°C at the rate of -10.00°C/min. The measured melting and recrystallisation temperatures are used for determining the process settings. The DSC analysis reported exhibits both the initial heating curve as well as the cooling curve, traditionally not reported. However, for the purpose of process development for SLS these curves show the most dominant characteristics considered.

The baseline for fundamental process variables such as laser power and scan speed was based on feedback via thermal imaging in the system during pilot experiments to consolidate polymer powder using single-layer line scans. The process optimisation followed the method of varying one influential parameter and keeping the remaining constant, as suggested by singh, et. Al. [5,6] A homogeneous part achieved by well-consolidating powder and true to the original geometry was the visual qualitative metric used to iteratively optimise the process parameters when fusing single-layer area scans. For process development, initial experiments were carried out using 50mm line scans followed by 10mm x 10mm area scans and finally, 10mm x 50mm area scans, i.e. identical to the test part geometry.

2.4. Conductivity qualification

To accurately measure the conductivity of the samples, a 4-wire (4W) measurement is preferred. The 4W measurement injects current through a set of contacts (Force) and measures voltage through a separate set of contacts (Sense). This separation between the Force and Sense contacts means that any contact resistance should be bypassed and hence the intrinsic resistance of the samples can be measured directly. A Keithley 2450 SourceMeter was used for the measurements. Each sample was measured 50 times, roughly 2 seconds apart. The mean of those 50 measurements was used for the conductivity calculation, which is done with the following equation:

$$\sigma = \frac{l}{RA}$$

Where σ is the apparent conductivity, l is the distance between the sense contacts, A is the cross-sectional area of the sample and R is the mean resistance described above.

3. Results

Several methods are used to determine the conductivity and possible sensor capabilities of the parts. The parts are quantified by microscopy providing additional information on the level of consolidation of the powder. These efforts are described below. All parts were allowed to condition in an open atmosphere for at least one week before the investigation of part stability and electrical conductivity.

3.1. Material production and qualification

A DSC analysis was carried out to indicate the process parameters of the material. The elevated chamber temperature was selected based on a DSC scan of the material as seen in Figure 1. The DSC analysis showed the primary material melting peak at 167°C, along with a small endothermic shoulder at 33-55°C. These are the other components of the designed polymer, providing the characteristics of the flexible conductive polymer part. The analysis also shows the crystallisation temperature of the main constituent polymer, at 128°C.

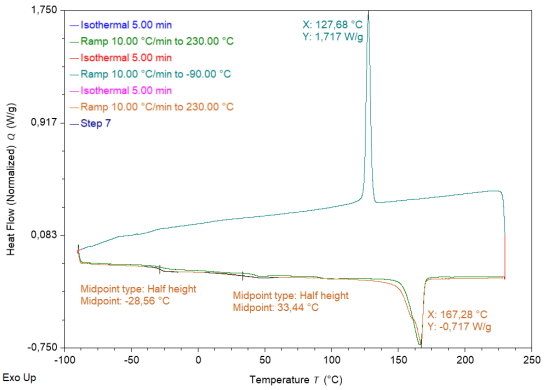

Figure 1 – DSC analysis of the PL-PBF tailored material

3.2. Powder characteristics

The processed powder was analysed by light optical microscope (LOM) and Scanning Electron Microscopy (SEM), to determine the morphology of the powder particles. Due to the nature of cryogenic ball milling, the main constituent of the powder is oblong flakes, as seen in Figure 2. These flakes cause issues in the spreadability of the powder, due to the adhesion and interlocking of the particles. This was evident in the heated process parameter test, where large agglomerates would disturb the powder bed. The agglomeration is further aided by the Vistamaxx component turning soft and sticky at the process temperatures. The powder contains a large number of small particles. The small particles are highlighted by the red circles in the SEM picture showing the variation in particle size. These particles also influence the agglomeration of the powder.

The powder particle sizes for the fine and coarse powders were analysed to have a D50 of 72,6 ± 0,182 µm and 290 ± 4,63

µm respectively. As seen from Figure 3 the fine powders include a fraction of very fine (<10µm) particles which add to the agglomeration of powders and hence a lower cut-off from the final powder will be carried out in powder production for future investigations.

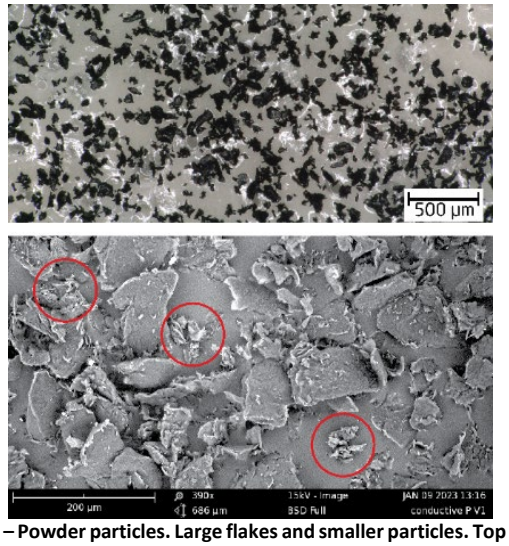

Figure 2 – Powder particles. Large flakes and smaller particles. Top 100x LOM picture. Bottom 390x SEM picture.

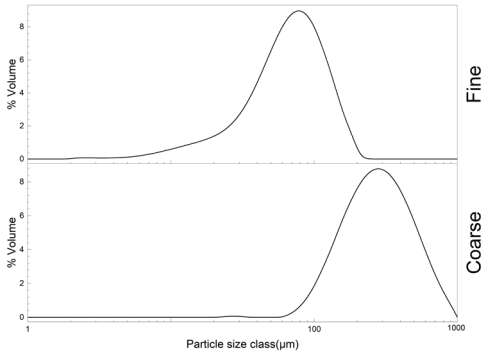

Figure 3 – Particle size curve of the manufactured powder. Fine is the sieved powder used for part manufacturing. Coarse is the discarded portion after sieving.

3.3. Process parameters

The process parameters developed for producing conductive parts were different by the chamber temperature, which is a key parameter of PL-LBF. The chamber temperature setting has a large influence on the laser power input required to achieve consolidation of the part. The level of internal stress is also reduced by elevating the chamber temperature minimising the risk of warpage and curling during laser scanning. The chamber temperature was set to 130°C for the heated sample manufacturing and left unheated for the other parameter set resulting in 20°C in the build chamber.

The elevated chamber temperature was selected based on a DSC scan of the material, as seen in Figure 1**.** The process window for the material proved to be rather large, extending from melting at 167°C to recrystallisation at 128°C. Vistamaxx softens at a temperature of around 50°C, according to the datasheet. The two polymer phases seem to be only partially miscible as seen from the small shoulder in the DSC around 50°C. This shoulder indicates the glass transition of the material. Thus, a small part of the Vistamaxx could be softening, causing a very sticky powder to be formed at elevated temperatures. Based on this, the preheating setting was chosen. The temperature setting allowed for minimal shrinkage during processing, while not producing a consolidated matrix from the entire powder cake.

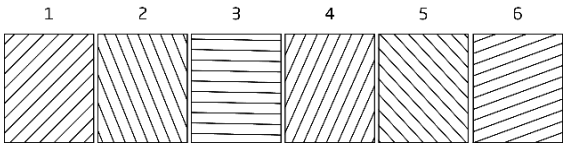

Figure 4 – scan strategy per scan pass from scan one to six

The process optimisation developed two process parameter sets for the two trials. The process parameters are seen in Table 1, showing the main difference in scanning speed. The resulting energy density is also presented in the Table, showing a reduction of 1/3 of the energy input between the unheated and heated run. This lower energy input still ensured consolidated parts that maintained dimension, during processing and after cooling to room temperature. The parts were produced by scanning the same part 6 times while rotating the scan direction 67 degrees. This variation in the scan direction is seen in Figure 4. This ensures consolidated parts while minimising the risk of unsintered particles or areas.

Table 1 – Process parameters

		Unheated	Heated
Scan Speed	mm/s	2000	3000
Power	W	30	30
Scan rotation	Degrees	67	67
Hatch spacing	µm	150	150
Scan repetitions		6	6
Energy density	J/mm^2	0,1	0,066

The production of parts was done in the atmosphere, leading to possible moisture ingress. The atmosphere is considered not to be problematic. The constituent materials are not prone to hydrolysis or other degradation caused by moisture uptake from the atmosphere. Furthermore, the powder is handled with minimised contact with the atmosphere before part manufacturing.

3.4. Part Characteristics

The parts manufactured showed large variation between the two process parameter sets. The unheated parts exhibited shrinkage and geometric variation compared to the intended size.

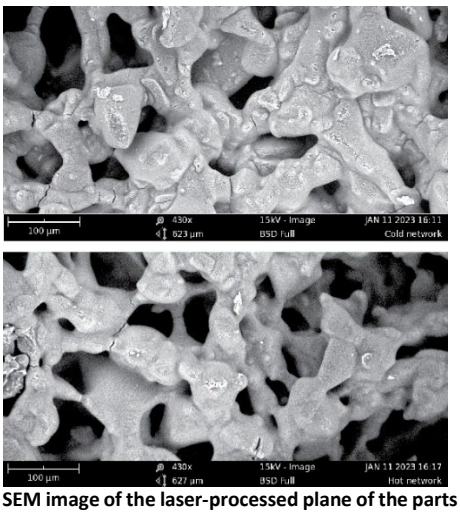

Figure 5 – SEM image of the laser-processed plane of the parts showing the comparison of the two networks for unheated (top) and heated (bottom)

The unheated parts were thinner than the heated ones with an average thickness of 373µm and 674µm, respectively. The variation in thickness is caused by energy penetrating deeper into the heated samples due to the lower loss of energy in the

initial powder layer, due to the increased temperature of the powder cake. The melting effect on the unheated and heated samples is also evident in the SEM picture in Figure 5 showing a smooth surface with less evidence of the powder particles in the heated sample compared to the unheated one. The melting behaviour and flow of the particles into a smooth network point towards the heated sample experiencing the melting of both polymers, with time above crystallisation long enough to flow. Where the tendency of the unheated sample points to only melting of one of the components. This is evident by the shape retention with the unheated part network resembling the powder structure.

3.5. Conductivity

The results from the conductivity measurement can be seen in Tables 2 and 3 for the heated and unheated samples respectively. Five samples were tested for each, however, one of the unheated samples tore completely before the measurement could be done.

The unheated samples were relatively consistent with samples B, C and D having similar apparent conductivity. Sample A, while having the highest conductivity overall, is assumed to be an outlier. The heated samples are more inconsistent. Sample A and B are very similar, as is sample C and E, but the two pairs are quite different from each other as well as sample D.

The measurement was done with crocodile clips. The cables used outweigh the samples and it is possible that the measurements were influenced by the strain put on the sample by the cables. Additionally, any tears in the samples due to the strain will have a significant influence on the measured resistance and conductivity.

Table 2: Heated samples

Sample	Resistance $[k\Omega]$	Area $[mm^2]$	Length $[mm]$	Conductivity $[mSm^{-1}]$
A	71,37	6,7	24,0	49,9
B	66,81	6,7	24,0	53,3
C	158,7	6,7	25,5	23,9
D	109,2	6,7	24,0	32,6
E	141,8	6,7	25,1	26,2
Avg/ std	109,6 / 41			37,2 / 13,6

Table 3: Unheated samples

Sample	Resistance $[k\Omega]$	Area $[mm^2]$	Length $[mm]$	Conductivity $[mSm^{-1}]$
A	101,3	3,0	23,32	77,1
B	132,8	3,0	21,08	53,2
C	137,5	3,0	20,97	51,1
D	133,2	3,0	22,63	56,9
Avg / std	126,2 / 16,7			59,6 / 11,9

4. Analysis

The parts manufactured were initially expected to be dense and not show porosity, however during the investigation of the parts, it was clear that the sintering process developed a network-like sponge. This sponge structure has a large influence on the structural integrity and the conductivity of the parts. The sponge structure develops due to the process not allowing the flow of material into the voids during the scanning. The material exhibits a high zero shear viscosity, which is known for most polymers [7]. Highly loaded composites typically show an increase in viscosity, with the carbon black loading known to cause this. The effect is evident when comparing the MFI of the two miscible polymers, with a significantly higher MFI reported for the carbon black loaded polyolefin compared to the Vistamaxx. This high viscosity causes the powder particles to stay in place even when molten due to the limited external forces, besides gravity acting on the powder. From the SEM pictures, it can be seen that the flow behaviour is improved in the heated samples with a smoothed surface of the network.

The conductivity of the parts is influenced by the network structure. The apparent conductivity for the unheated samples is higher than for the heated samples. However, both process parameters created parts with large variations, proving that the powder, packing and process should be further optimised. The higher conductivity of the unheated parts can be due to the Vistamaxx polymer having a lower viscosity allowing a flow of the material and creating a network that is more ductile causing a better conductivity in the network after the parts have been handled in the measurement setup. The flow behaviour and optimisation of the process and powder are planned for future experiments.

5. Conclusion

Manufacturing of parts which show conductivity when measured using the 4W approach was successful. From these parts, a simple sensor function can be expected. However, from the network structure seen by SEM pictures, it is clear that the manufacturing process needs to be optimised. This includes consideration of the material and the zero shear viscosity, and the powder manufacturing, making a more uniform and less flaky powder. As well as finding an even more suitable set of process parameters.

The two parameter sets both proved viable for producing parts. The result is conflicting with the heated samples showing the highest geometric and structural stability, with an internal network that has been smoothed during manufacturing. These samples, however, also show the lowest conductivity with the standard deviation being more than 1/3 of the average apparent conductivity. The unheated samples were showing a better average apparent conductivity with a smaller standard deviation in the measurements. These parts were highly irregular, showed large shrinkage and a not fully melted network.

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