Surface Modification of Additively Manufactured Parts Using an Atmospheric Pressure Plasma

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Abstract: One of the most common types of additive manufacturing, fused filament fabrication (FFF) suffers from poor interlayer adhesion, which significantly limits this technique for creating functional parts. Treatment of parts with an atmospheric plasma array during printing shows over 100% improvement of the bond strength compared to parts without plasma treatment by a shear bond strength test. The mechanisms for the bond improvement is investigated.

Keywords: Additive manufacturing, bonding strength, surface modification.

1. Introduction

With the continuing decline in price of thermoplastic extrusion printers, fused filament fabrication (FFF, also known as fused deposition modelling, FDM, a name trademarked by Stratasys) is becoming one of the most common types of additive manufacturing. A part is created by heating a thermoplastic above its glass transition temperature and extruding it through a nozzle attached to a movable head. A layer is created and then moved so that another layer can be deposited on top of it. This process repeats until the entire part has been created [1]. Despite its nearly unlimited versatility in creating geometric parts, one of the largest hurdles that hinders FFF is the weak bonding between subsequent layers. This is because the interlayer bonding is much weaker compared to the lateral direction along the bulk material fibers.

Numerous attempts have been made to mitigate the weak z-strength of the interlayer bonding. Some have tried optimizing the printing parameters [2], while others have tried changing materials [3]. Energy addition external to the printing process has also been used to help maintain the temperature of the printed part, such as using a laser to melt the top layer prior to printing another layer [4], or using microwave heating [5].

This work focuses on a continuation of work done using a low temperature atmospheric plasma to modify the surface of a 3D printed part [6]. This approach is different in that it focuses on relatively long lived non-thermal modification to the surfaces as opposed to the predominately thermal melting effects of other techniques.

The nature of the plasma source may affect the resulting surface chemistry. This source exploited numerous effects to achieve a low temperature treatment, including 1) nanosecond pulses to avoid a possible time-dependent transition in the plasma with increasing current, such as a glow-to-arc transition; 2) gas flow to enhance convection and in particular using helium with its favourable electrical and transport properties [7-8]; 3) a corona discharge geometry using the sharp tips to localize the electric field while having an incomplete breakdown of the gas gap [9]; and 4) a dielectric barrier discharge, using the dielectric of the 3D printed part to limit the current [10].

2. Experimental Setup

A Dreamer 3D printer (Flashforge, Zhejiang, China) was used to print a polylactic acid (PLA) plastic block measuring 20 mm by 12.5 mm by 12.5 mm. The printing was then paused and the printing platform was removed for plasma treatment. Removal was necessary to avoid electromagnetic interference during the plasma treatment. After plasma treatment, the printing platform was reinstalled and allowed to come back to thermal equilibrium with the bed temperature. A second layer measuring 10 mm by 12.5 mm by 0.9 mm was printed over half of the block. A schematic of the entire printed block is seen in Figure 1(a).

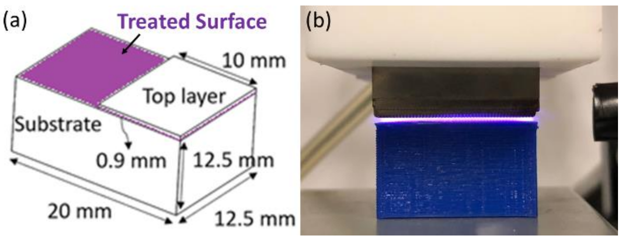

Figure 1: Schematic of the printed part (a) and plasma treating of the part (b)

The plasma treatment (Figure 1(b)) was done using a high voltage nanosecond pulser, FPG 30-N (FID GmbH, Burbach, Germany), run at a voltage of 20 kV, with a pulse width of 3 ns, at a pulse frequency of 2 kHz. The energy per pulse was measured to be approximately 0.5 mJ. The electrode used consisted of an array of sharp tips with gas spacers. The tips were spaced 0.5 mm apart along 0.6 mm thick sheets created by electrode discharge machining (EDM). Each EDM sheet was separated by a

0.4 mm gap of U-shaped spacers to allow gas flow through the array. The sheets of tips and spacers were then partially enclosed in a Teflon holder to hold them together and allow connection to both the high voltage pulser and a gas bottle. Helium (99.9%) was used as the working gas, flowing at 2.5 SLPM into ambient air. The electrode-to-3D printed part gap was maintained at 1 mm. All testing was done at ambient temperature and pressure (approximately 22°C and 1 atm).

Spectra was acquired using a spectrometer (Ocean Optics HR4000 High-resolution spectrometer) using a 1 s integration time. Using SpecAir [11-12] the rotational and vibrational temperatures were determined for the second positive system of nitrogen, which comes from the ambient air mixing with the helium gas flow through the array.

Four main conditions were tested against a control: two plasma treatment times (30 s and 300 s, denoted CPT30 and CPT300 in figures), a polished surface, and a polished and plasma treated surface (300 s treatment, denoted P+CPT). The polishing was done by 180 grit sandpaper and cleaned with compressed air. The polished case was used as a control for an improved wettability case without functionalizing the surface chemically.

A custom apparatus was built to test the shear force required to peel off the top layer of the printed part (Figure 2). The shearing tip of the apparatus was moved linearly at 12.5 mm/min against the base block and the force to shear off the second top layer was measured using a dynamometer. Scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) were used to investigate the surface changes of the thermoplastic due to the plasma treatment.

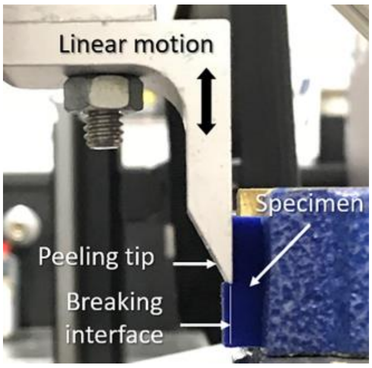

Figure 2: Shear bond strength testing apparatus

3. Results and Discussion

The rotational and vibrational temperatures for this discharge were modelled to be approximately 362 K and 3248 K, respectively (Figure 3). The discharge was highly non-equilibrium due to both its nanosecond pulse duration and the thick dielectric (that is the 3D printed part) acting as the ground electrode.

The results from the shear bonding strength are shown in Figure 4, where the error bars are the standard error for a sample size of 5 tests for each condition. The 30 s plasma treated samples show more than a 100% increase in the shear force required to remove the top layer. However bonding strength does not increase with treatment time, since the 300 s treatment has a lower shearing force than the 30 s treatment. Polishing the surface did not improve the bonding strength, despite the polished surface being the surface with the highest wettability. Plasma treating the polished surface also did not change the bonding strength.

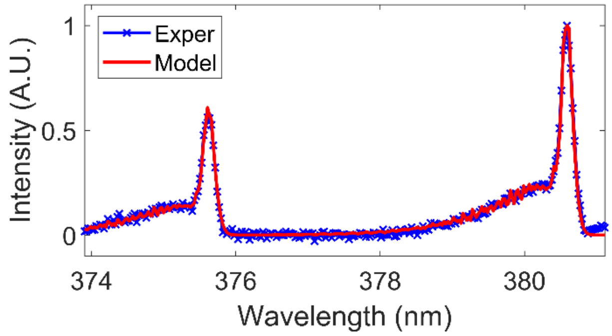

Figure 3: Experimentally measured and SpecAir modelled spectra of the discharge

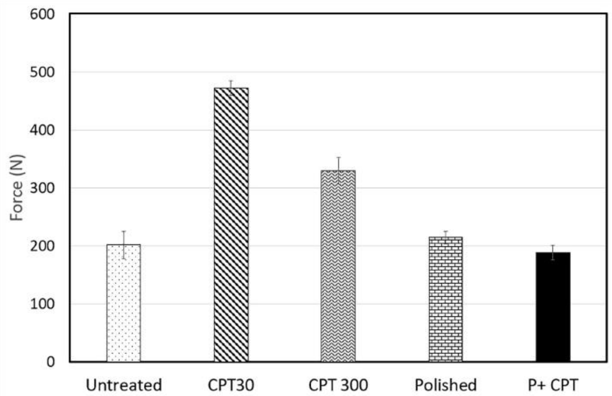

Figure 4: Shearing force required to remove the top 3D printed layer

Optical microscopy of the fractured surfaces yielded stress whitening in the two plasma treated cases without polishing (Figure 5), but was absent in the untreated and both polished cases (with and without plasma treatment). The small white marks noted in the polished samples came from the polishing and not the delamination process. Stress whitening occurs when a tensile load creates micro-voids in the material due to the movement of molecular chains, which causes a change in the material's refractive index. The degree of the whitening can also show the level of the bonding force between layers after delamination. This suggests that the plasma treatment helped in chemically bonding the subsequent layers to the base part.

Due to the high viscosity of the extruded material, the increase in wettability of the polished part did not have any significant effect, while the plasma treatment greatly increased the bond strength. Multiple effects could be the cause of the increased strength, including modifying the surface nanostructure, extracting hydrogen thus creating dangling bonds, or oxidizing the surface of the polymer. A combination could also occur, initially causing the improvement of the bond strength with plasma treatment but having further treatment degrade the strength improvement and explaining why the 300 s treatment yielded a lower strength than the 30 s treatment. Further study using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) is expected to further explain this phenomenon.

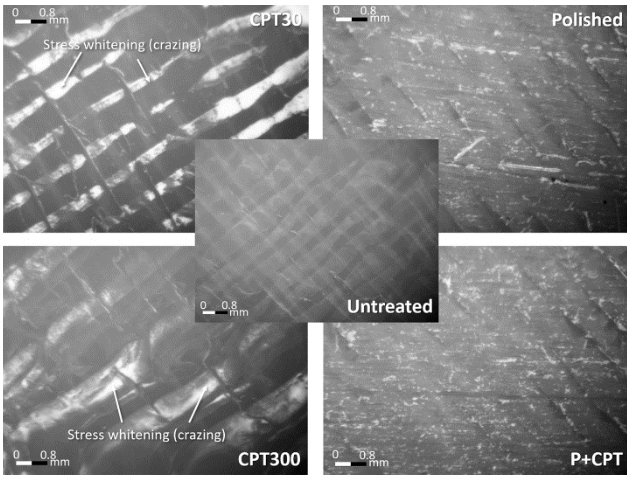

Figure 5: Optical micrographs of the sheared surface for the various treatment conditions

4. Conclusions

Low temperature, atmospheric plasma treatment was shown to improve the interlayer bonding strength of a PLA part by over 100%, bringing the z-direction strength closer to that along the transverse x- and y-directions. Optical microscopy along with the shear bonding strength of the various conditions suggests that wettability does not contribute to the strength improvement. Other possible effects are explored to explain the improved strength stemming from the plasma treatment.

5. References

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