Heat treatment of 3D printed polyethylene terephthalate glycol in a supporting powder bed

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Abstract. Material extrusion 3D printing is a fabrication process that produces layered polymer parts with complex geometry but with inferior mechanical properties compared to parts made with other methods such as injection molding. Post fabrication heat treatment is a valid post-processing method that reduces the internal thermal stresses and improves layer adhesion in 3D printed polymers, resulting in superior mechanical properties. This study investigates the mechanical changes produced in 3D printed PETG (polyethylene terephthalate glycol-modified) parts after heat treatment. A novel technique is used, where the parts are embedded into a bed of sodium chloride powder in order to prevent deformation during post-processing. Fully filled 3D printed PETG parts with various geometries are tightly packed in a bed of powder. The parts are subjected to heat treatment at a temperature above the material’s glass transition temperature but below its melting temperature. Destructive and non-destructive testing performed on the treated 3D printed samples shows a substantial improvement of mechanical properties. Tensile strength testing reveals an increase of tensile strength by 40% for parts printed horizontally and by over 100% for parts printed vertically. Increased stiffness is also observed in treated parts. Compressive strength testing shows a strength increase of 43% after treatment. Dimensional measurements made prior to and after treatment show significantly reduced deformation when using the supporting powder method versus unsupported treatment. Scanning electron microscopy (SEM) analysis is used to assess internal structural changes in the polymer after post-processing. This analysis reveals changes in internal void shape and distribution, increased interlayer adhesion and increased interface area of deposited filaments, providing insight into the mechanisms that lead to the improved properties observed in destructive testing. The supporting powder heat treatment allows the fabrication of parts with complex geometry through material extrusion 3D printing while mitigating the inherent disadvantage of the fabrication process of producing parts with inferior mechanical properties.

1. Introduction
Additive manufacturing (AM) is a growing industry forecast to expand by double digit compound annual growth in the upcoming years through 2028 [1]. Material extrusion 3D printing (ME3DP) is an AM process that produces layered polymer parts with complex geometry but with inferior mechanical properties compared to parts made with other methods such as injection molding. Following the expiration of patents held by Stratasys in 2009, fused deposition modelling (FDM / ME3DP) has seen wide adoption with home users, public institutions and businesses of all sizes [2, 3].
In ME3DP fabrication of a part begins with creating a digital 3D model of the part followed by sectioning this 3D model into thin layers using a dedicated software program called a slicer. Each layer’s surface is filled using a trajectory that takes into account various process parameters, such as the number of perimeters, part infill (how much of the part internal volume will be made of solid material), infill pattern, infill overlap, air gap. A 3D printer that uses this process uses thermoplastic polymers as feedstock. The material in the shape of filament or pellets is extruded through a heated nozzle and deposited in layers onto a horizontal surface called a bed or a build plate. The material liquefies in the heated nozzle and solidifies after extrusion due to convective cooling with the surrounding air and due to conductive cooling by coming in contact with the bed or previously deposited material. The extruder moves relative to the bed in the horizontal plane, according to the trajectories calculated by the slicing software for each layer.

The layered aspect of 3D printing results in inherent flaws in the fabricated parts using an FDM process. As thermoplastic polymer begins cooling down after extrusion through the heated nozzle, internal thermal stresses develop inside the part [4], leading to reduced mechanical properties compared to injection moulding processes [5]. More so, filaments are being deposited at a significantly higher temperature than the underlying layers, leading to improper interlayer adhesion. This is also the case for deposited adjacent filaments, but to a lesser extent. For this reason, 3D printed parts exhibit an anisotropic behaviour where the mechanical resistance on the Z axis (perpendicular to the build plate) is inferior to that on the X and Y axis (parallel to the build plate) [6, 7]. Additionally, the extrusion nozzles used to deposit material have round bores, meaning not all horizontal surfaces can be covered fully to form uniform layers of material. Thus, complex curves, narrow angles and other geometric features of the horizontal layers lead to the formation of internal voids. Due to the repetitive patterning aspect of filling a layer, these voids align forming a failure point in the printed part [8, 9].

Heat treatment is a post-processing method used to improve mechanical properties of thermoplastic polymer parts. By applying heat to a printed part, the internal thermal stresses generated during part fabrication can be balanced. At a molecular level, heat treatments can promote polymer crystallization resulting in higher tensile strength and stiffness [10, 11]. However, heat treatment also comes with a significant and hard to overcome disadvantage. As a consequence of reducing the internal thermal stresses and the changes in molecular structure of the material, deformation of the parts during treatment is often encountered [12, 13]. This study proposes a novel method of packing polymer 3D printing parts in a supporting powder that prevents deformation during heat treatment.

Polyethylene terephthalate glycol-modified (PETG) is a mostly amorphous polymer that has a low degree of crystallinity [14] and a melting temperature between 240 °C and 260 °C. It is derived from the widely used polyethylene terephthalate (PET) polymer through the addition of a glycol group to the polymeric chain and shares many of its properties [15]. The addition of glycol improves flowability and lowers the glass transition temperature, making it better suited for using in 3D printing processes.

2. Methods and materials
This study focuses on the changes observed in mechanical properties of PETG, more specifically, tensile and compressive characteristics, following heat treatment. The feedstock material used for experimentation comes in the form of 1.75 mm diameter filament and is supplied by 3D Prima (Malmö, Sweden). According to the product datasheet, the material has a glass transition temperature of 75 °C and a recommended extrusion temperature of 230 °C to 255 °C. The material is transparent, with no added pigments or dyes.

The heat treatment consists in raising the temperature of the printed samples to 220 °C, a temperature that is well above the glass transition temperature of the material, and slightly under the melting temperature of the polymer. Once the parts have reached the target temperature, the
temperature is maintained for 15 minutes. The procedure begins with fabricating the 3D printed parts, with each printing job producing one sample. After printing, the parts are placed in a borosilicate glass container lined with supporting powder (figure 1c). The samples are placed at a minimum of 10 mm off the edges of the container and at least 10 mm of space is left between the samples. The supporting powder is grounded sodium chloride with particles ranging between 10 μm and 50 μm. After placing the samples, more powder is used to fill the gaps between them. The powder is tightly packed using a rubber mallet, making sure that no empty spaces are left around the samples. NTC thermistors are inserted near the packed parts to track temperature changes. The container with the packaged samples is then introduced in a convection oven preheated to 220 °C (figure 1d). Once the sensors readout reaches the treatment temperature, a 15-minute timer is started. The package is removed from the oven once the timer elapses and it is left to cool at room temperature. After cooling, the samples are unpacked and washed with room temperature clean water to remove any powder residue.

For tensile strength tests 20 samples have been designed and fabricated according to ASTM Type I standard dimensions (figure 1a). The samples have been 3D printed with 2 outside perimeters, 100% infill, 25% infill overlap and an alternating 45° grid infill pattern. The nozzle used is 0.4 mm in diameter and the extrusion temperature was set at 235 °C. Two orientations are used, one in which parts are placed horizontally on the build plate, and one where the parts are placed vertically. The layer height for all 3D printed samples is 0.2 mm.

After 3D printing, the parts have been separated into four groups, each consisting of five samples. Two groups represent parts that undergo heat treatment, one for each orientation, while the two remaining groups are control groups that undergo destructive testing without heat treatment.

For compressive strength tests, cube samples with a width of 15 mm have been manufactured using the same process parameters described previously (figure 1b). These samples are divided into two groups, one undergoing heat treatment and one untreated control group. All printed samples were fabricated on a Creality Ender 3 machine supplied by Shenzhen Creality 3D Technology Co., Ltd (Shenzhen, CN). The machine is a Cartesian 3D printer with a moving build plate along the X axis and Bowden-fed extruder that moves along the Y and Z axis.

Destructive testing was done on an Instron 8872 (Norwood, MA, USA) universal testing machine (figure 1g) at a loading speed of 10 mm per minute and a preload tension (or compression) force of 5 N. Tensile strength tests also tracked sample elongation under strain using a contacting extensometer. For compressive strength tests the cube shaped samples have been placed in such a way that the compressive load is applied perpendicular to its horizontal printed layers (along the sample’s Z axis).
SEM analysis was used in order to inspect the internal changes occurring in the structure of the materials after heat treatment. For this analysis, samples were selected from the treated and control groups and imaged using a Quanta Inspect F50 FEG (Field Emission Gun) scanning electron microscope with 1.2 nm resolution. The microscope is equipped with an energy-dispersive X-ray (EDX) analyzer with a resolution of 133 eV at MnKα from Thermo Fisher Scientific (Eindhoven, The Netherlands). All investigated samples were covered with a slim layer of gold using the Q150 Plus Series sputter coating machine from Quorum Technologies (Lewes, UK). The sample coverage time was 30 seconds.

3. Results

3.1. Dimensional changes
For samples 3D printed and heat treated at 220 °C in open air, dimensional changes range between 2.1% for the Z axis (corresponding to the vertical axis during printing process) and 1.3% for the X and Y axis (horizontal plane). For the sample group treated in supporting powder, the dimensional changes are significantly lower, ranging from 0.4% for the Z axis (vertical axis) and 0.3% for the X and Y axis (horizontal plane). No curvature was observed in the dogbone-shaped samples after the supportive powder heat treatment. These observations indicate that the powder method is effective at supporting samples during heat treatment and reducing dimensional changes.

3.2. Tensile strength and stiffness
Fractographic analysis shows the vertically printed samples broke along the layer interfaces (figure 2d, e). For untreated samples printed in horizontal orientation (figure 2c), the fractures happened along the 45° raster infill. The heat-treated horizontal samples experienced a more ductile failure, with necking occurring in some samples (figure 2a).

![Figure 2. Compressive strength testing results: (a, b) horizontal, treated, (c) horizontal, untreated, (d) vertical, treated; (e) vertical, untreated.](image)

Heat treated samples show a significant increase in tensile strength compared to the control group. For parts 3D printed in a horizontal orientation, the tensile strength of 43.8 MPa is 40% greater than the control group (figure 3). For samples 3D printed in a vertical orientation, the improvement in tensile strength is much higher, treated samples resisting a tensile load of 35.9 MPa before failing, compared to 15.6 MPa in the control group, a 130% increase (figure 4). Figure 5 shows a comparison of tensile testing results for parts printed in the two different orientations.

An increase in sample stiffness can also be observed (figure 6). Young’s modulus for horizontally printed samples is 13.5% higher in the treated group (1863 MPa) compared to the control group (1641 MPa). For vertically printed samples, the increase in stiffness is 21.7% (1944 MPa vs 1597 MPa).
Figure 3. Tensile testing results for parts printed in horizontal orientation.

Figure 4. Tensile testing results for parts printed in vertical orientation.

Figure 5. Tensile strength of sample groups.

Figure 6. Young’s Modulus of sample groups.

3.3. Compressive strength

A change in failure mode is observed after heat treatment, with the samples in the treated group experiencing more interlayer shearing under compressive load. Similar to the increase in tensile strength, heat treatment improved compressive strength as well. The cube-shaped samples in the test group failed under compressive load at 101.9 ± 7.8 MPa compared to 70.9 ± 11.2 MPa for the control group. This translates to an average increase of compressive strength of 43%. The results of these tests are shown in figure 7.

Figure 7. Compressive strength testing results.
3.4. Internal structural changes
Scanning Electron Microscopy imaging gives insight into the reasons behind the observations made following destructive testing experiments. Figure 8 shows images taken of an untreated sample printed in horizontal orientation. As revealed by the fractographic analysis, the sample ruptured in a zig-zag pattern along the 45° infill directions. Material necking can be observed near the fracture surface, an indication that the sample failed prematurely because of shearing between adjacent filaments. The necking occurs due to differences in the molecular structure of deposited filaments developed during fabrication. After extrusion through the heated nozzle, the exterior surfaces of the filaments cool through convection with ambient air and through conduction with the previously deposited material [16]. At the same time, the core of the filament cools down slower, as it is limited by the thermal conductivity of the material. The images show limited adhesion between adjacent filaments and almost no material diffusion. Micro-voids 50 μm to 80 μm in width can be seen at the interface between successive layers and are largely caused by the transition of infill direction from 45° to -45°. These micro-voids have a compounding effect and are very detrimental to the part’s structural strength because of their patterning aspect. Figure 9 shows a test sample printed in the same orientation, with the same process parameters, that has undergone heat treatment. It is immediately obvious that the heat treatment resulted in increased adhesion and diffusion between adjacent filaments. The interfaces between filaments are elongated and necking is reduced, a sign that the macrostructure has become more resistant to shearing loads developed between adjacent filaments. As the material was heated past its glass transition temperature, molecular motion causes the coalescence and the reduction in size of the micro-voids inherent to the fabrication process. The micro-voids measure between 20 μm and 40 μm in the treated part.

Figure 8. SEM imaging of control sample printed in horizontal orientation: (a) microvoids; (b) poor filament adhesion.

Figure 9. SEM imaging of treated sample printed in horizontal orientation showing increased diffusion between filaments.

Figure 10 shows images captured of a sample printed in the vertical direction from the control group. As revealed by the fractographic analysis, the samples failed at the interface between layers due to poor interlayer adhesion. Unlike the horizontally printed samples, where the tensile load has a
component along the filament length, the strength of vertically printed samples is largely determined by interlayer adhesion. As mentioned previously, the adhesion between deposited filaments depends on the temperature difference between them. During fabrication the extrusion temperature is constant, but previously deposited filaments cool down at different rates, depending on their position in the part. Thus, when fresh material is extruded, the largest temperature difference will be with filaments deposited in the previous layer, as these are the filaments that had more time to cool down through convective and conductive effects. For this reason, this sample group performed the worst during destructive tensile strength testing. Additionally, a low amount of material diffusion between adjacent filaments can be seen. Large internal voids, over 150 μm in size can be seen at the intersection between the infill in the exterior contours.

Figure 11 shows images from of a treated sample printed in the vertical direction. Flaking can be seen in various areas of the fracture surface, indicating fracture lines across multiple horizontal layers. This is a clear sign interlayer adhesion has increased compared to the part from the control group [17]. Due to the material being heated over its glass transition temperature, molecular mobility has increased and internal voids have migrated and coalesced, reducing the patterning compounding effect. A change in the shape of the micro-voids is also evident. The voids are more spherical compared to the obloid and elongated voids present in the control group sample.

![Figure 10. SEM imaging of control sample printed in vertical orientation.](image)

![Figure 11. SEM imaging of treated sample printed in vertical orientation.](image)

4. Discussions and conclusions
This research seeks to investigate whether heat treating PETG parts in a supporting powder bed is a viable method of improving their mechanical properties. Twenty dogbone samples and 10 cubic samples were 3D printed from PETG polymer. The samples were split into groups according to part orientation during fabrication and 10 dogbone samples and 5 cubic samples were heat treated in a bed of supporting powder and then put through tensile and compression strength testing. Dimensional measurements made prior to and after treatment show significantly reduced deformation when using the supporting powder method versus unsupported treatment. Samples from all treated groups saw increases in mechanical performance over the control groups. For dogbone samples printed...
horizontally, heat treatment increased tensile strength by 40% and stiffness by 13.5%. For samples printed vertically, the increases are more significant, with tensile strength increasing by 130% and stiffness increasing by 21.7%. On cubic samples compressive strength increased by 43%.

SEM analysis revealed that raising and maintaining the temperature over the glass transition temperature for 15 minutes has caused important changes in the 3D printed part internal structure. Increasing molecular mobility through heating resulted in better diffusion of material between adjacent filaments leading to less shearing susceptibility. This is also highlighted by the fact that less localized necking is present at the fracture interface. After heat treatment, the internal micro-voids migrated and coalesced, reducing the patterning effect that results in the forming of failure points.

The results obtained in this study point to significant improvements in mechanical properties that offset the inherent anisotropic character of 3D printed parts. This is of major importance for parts with complex geometry that are required to be strong in more than one direction. At this point, the applicability of the process has been demonstrated on simple geometric shapes such as test specimens and on small objects with complex geometric shapes. The process is expected to function for a wide range of part geometries and has similarities to fabricating using moulds and casting. During treatment, the exterior surfaces of the parts see an increase in roughness that is correlated to the choice of powder material. More research is required to identify other suitable powders.

5. References

[1] ReaserchandMarkets.com 2020 Global Additive Manufacturing Market and Technology Forecast to 2028 Market Report ID 5144559.

[2] Steenhuis H-J and Pretorius L 2016 Consumer additive manufacturing or 3D printing adoption: An exploratory study J. Manuf. Technol. Manag. 27, 990–1012.

[3] Sepasgozar S M E, Shi A, Yang L, Shirowzhan, S and Edwards D J 2020 Additive Manufacturing Applications for Industry 4.0: A Systematic Critical Review. Buildings 10 231.

[4] Costa S F, Duarte F M and Covas J A 2015 Thermal conditions affecting heat transfer in FDM/FFE: A contribution towards the numerical modelling of the process Virtual Phys. Prototyp. 10 35–46.

[5] Priya M S, Naresh K, Jayaganthan R and Velmurugan R 2019 A comparative study between in-house 3D printed and injection molded ABS and PLA polymers for low-frequency applications. Mater. Res. Express 6 085345.

[6] Ahn S-H, Montero M, Odell D, Roundy S and Wright P K 2002 Anisotropic material properties of fused deposition modeling ABS Rapid Prototyp. J. 8 248-57.

[7] Sood A K, Ohdar R K and Mahapatra S S 2010 Parametric appraisal of mechanical property of fused deposition modelling processed parts Mater. Des. 31 287–95.

[8] Rodriguez J F, Thomas J P and Renaud J E 2000 Characterization of the mesostructure of fused-deposition acrylonitrile—Butadiene—Styrene materials. Rapid Prototyp. J. 6 175–86.

[9] Amza CG, Zapciu A, Eyrósdóttir A, Björnsdóttir A, Borg J 2019 Embedding Ultra-High-Molecular-Weight Polyethylene Fibers in 3D printed Polyactic Acid (PLA) Parts Polymers 11 1825.

[10] Butt J and Bhaskar R 2020 Investigating the Effects of Annealing on the Mechanical Properties of FFF-Printed Thermoplastics. J. Manuf. Mater. Process. 4 38.

[11] Hart K R, Dunn R M, Sietins J M, Hofmeister Mock C M, Mackay M E and Wetzel E D 2018 Increased fracture toughness of additively manufactured amorphous thermoplastics via thermal annealing Polymer 144 192–204.

[12] Slavković V, Grujović N, Dišić A and Radovanović A 2017 Influence of Annealing and Printing Directions on Mechanical Properties of PLA Shape Memory Polymer Produced by
Fused Deposition Modeling Proceedings of the 6th International Congress of Serbian Society of Mechanics (Mountain Tara, Serbia, June 19–21, 2017).

[13] Wijnen B, Sanders P and Pearce J M 2018 Improved model and experimental validation of deformation in fused filament fabrication of polylactic acid Prog. Addit. Manuf. 3 193–203.

[14] Dupaix R B and Boyce M C 2005 Finite strain behavior of poly(ethylene terephthalate) (PET) and poly(ethylene terephthalate)-glycol (PETG) Polymer 46 4827–38.

[15] Paszkiewicz S, Szymczyk A, Pawlikowska D, Irska, I, Taraghi I, Pilawka R, Gu J, Li X, Tu Y, Piesowicz E 2017 Synthesis and characterization of poly(ethylene terephthalate-co-1,4-cyclohexanediethylene terephthalate)-block-poly(tetramethylene oxide) copolymers RSC Adv. 7 41745-54.

[16] Morales N G, Fleck T J, Rhoads J F. 2018 The effect of interlayer cooling on the mechanical properties of components printed via fused deposition Addit. Manuf. 24 243–248.

[17] Gao X, Qi S, Kuang X, Su Y, Li J and Wang D 2021 Fused filament fabrication of polymer materials: A review of interlayer bond Addit. Manuf. 37 101658.

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