Tensile strengths of polyamide based 3D printed polymers in liquid nitrogen

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Abstract. Advances in additive manufacturing technology have made 3D printing a viable solution for many industries, allowing for the manufacture of designs that could not be made through traditional subtractive methods. Applicability of additive manufacturing in cryogenic applications is hindered, however, by a lack of accurate material properties information. Nylon is available for printing using fused deposition modeling (FDM) and selective laser sintering (SLS). We selected 5 SLS (DuraForm® EX, DuraForm® HST, DuraForm® PA, PA 640-GSL, and PA 840-GSL) and 2 FDM (Nylon 12, ULTEM) nylon variants based on the bulk material properties and printed properties at room temperature. Tensile tests were performed on five samples of each material while immersed in liquid nitrogen at approximately 77 Kelvin. Samples were tested in XY and, where available, Z printing directions to determine influence on material properties. Results show typical SLS and FDM nylon ultimate strength retention at 77 K, when compared to (extruded or molded) nylon ultimate strength.

1. Introduction
3D printing offers a new method of manufacturing thermoset and thermoplastic polymers. Deviations from well-known bulk material properties caused by this new method have yet to be extensively characterized at cryogenic temperatures, preventing adoption by the cryogenic industry. Polymers offer an alternative to conventional metal components due to lower thermal conductivity, density, and cost – ideal for lightweight insulating designs at a variety of temperatures. In many cases, bulk strength of these polymers increases as temperature drops to cryogenic levels [1,2], further improving their usefulness. However, very little material property information is available for 3D-printed materials at cryogenic temperatures.

Material, printing method, and print orientation contribute significantly to strength properties of printed plastics and are examined in this study. Strength of printed specimens is dependent on material and print orientation [3] and ultimately dictate the overall performance of a printed design. Two primary directions were studied for each material: (1) XZ plane and (2) ZX plane for FDM samples; (1) XY plane and (2) ZX plane for SLS samples. We anticipated that the anisotropic properties are significant in determining how materials react to loads at low temperatures.

2. 3D-printing technologies examined
2.1. Fused deposition modelling (FDM)
FDM is one of the most popular methods used today – especially in unmanned aerial vehicle (UAV) and space applications. A model is fabricated by extrusion of a thermoplastic material in a semi-molten phase onto a stage one layer at a time. At times, FDM models contain internal defects caused by the filament diameter and density affecting how the thermoplastic is extruded from the nozzle. The advantage of FDM lies in the ability to design a model using multiple materials as well as an ability to expand beyond conventional materials such as polycarbonate (PC) or acrylonitrile butadiene styrene (ABS) to glass reinforced polymers, metals, and ceramics [4].

2.2. Selective laser sintering (SLS)
SLS is a powder-based form of fabrication that has a wide array of engineering-grade materials available unique to the SLS printing method. SLS uses a high power laser to sinter polymer powders rather than using a liquid binder. Common materials are PC, polyvinyl chloride (PVC), ABS, nylon, resin, and polyester. Unlike FDM, SLS does not require scaffold support during the forming process, significantly saving on material cost; however, SLS models often suffer shrinkage and deformation from thermal expansion and cooling [4].

3. Materials and Methods
Stratasys Ltd. provided tensile specimens of FDM-printed Nylon-12 and ULTEM. Paramount Industries provided SLS-printed Duraform EX, Duraform HST, Duraform PA, carbon-glass reinforced nylon-12, and nylon-11. All specimens were manufactured according to ASTM D638 – Standard Test Methods for Tensile Properties of Plastics, Type I specimen. Five specimens were 3D printed for each test. FDM samples were tested in XZ and ZX orientations based off of the data we had from 3D printed material manufacturer specifications at room temperature. SLS materials were tested in XY and, where available, ZX orientations. KFH-6-350-C1-11L1M2R pre-wired Omega strain gauges were selected based on ASTM D638 recommendations and attached using cyanoacrylate. Strain gauges were set up using a type 1 quarter bridge with a thermal strain compensating dummy gauge fixed to a non-loaded segment in the same material immersed in liquid nitrogen. Strain from a quarter bridge arrangement is determined by

\[ \epsilon = \frac{-4V_r}{GF(1+2V_r)} \left( 1 + \frac{R_L}{R_g} \right) \]  

Where \( V_r \) is the ratio of measured voltage output to excitation voltage, \( GF \) is the gauge factor specified by the strain gauge manufacturer, and \( R_L \) and \( R_g \) are the lead wire and strain gauge resistances, respectively. The gauge factor for the KFH-6-350-C1-11L1M2 is 2.04 and the ratio of \( R_L/R_g \) = 0.001. Elastic modulus was determined from the slope of the stress vs strain relationship in one direction only, not using an hysteresis curve when estimating elastic modulus. Stress was computed from the measured load divided by the measured cross-sectional area of each specimen. Strain was calculated using the measured voltage per equation 1. The average measured cross sectional areas of the specimens is provided in Table 1.

| Material          | \( A_0 \), \( 10^{-5} \text{ m}^2 \) |
|-------------------|-------------------------------------|
| FDM Nylon-12      | 3.43                                |
| FDM ULTEM         | 3.46                                |
| SLS Duraform EX   | 3.28                                |
| SLS Duraform HST  | 3.33                                |
| SLS Duraform PA   | 2.93                                |
Specimens were mounted in 350 mL disposable cups prior to testing. Slits made for mounting were sealed using Devcon 5-minute epoxy. In order to prevent yielding at the tabbed regions, a funnel system was rigged to provide a constant stream of LN2 at both the top and bottom tabs (Figure 1). Tensile test measurements were conducted using a 4.45 kN load cell on a 49 kN Instron load frame at a constant-crosshead speed of $2.0 \times 10^{-3}$ cm/s. LN2 was added until thermal stress reached steady state then the specimens were axially loaded while LN2 was continually added to keep the specimen submerged until failure. Liquid nitrogen was also ported to the specimen clamps in an attempt to maintain uniform material temperature. Temperature sensors were not mounted on the specimen so we could not record the precise temperature.

**Figure 1.** Mounted specimen prepared for tensile testing.

### 4. Results

Ultimate tensile strength and modulus are reported by specimen print orientation. The 77K ultimate tensile stress values increased for all plastics except for FDM Nylon-12 which decreased by 0.4% in the XY direction and decreased by 21% in the Z direction (figure 2).
Figure 2. 77K mean ultimate stress and standard error. Black bars represent 3D printed material manufacturer’s room temperature values.

Modulus increased for all plastics at 77 K, as shown in figure 3. Change in modulus at 77 K from room temperature is shown in Table 3.

Figure 3. 77K mean modulus and standard error. Black bars represent material manufacturer’s room temperature values.
Table 2. Ultimate stress and elastic modulus at 77K for XY/XZ and ZX print directions. Material manufacturer specification values are given in parentheses for comparison.

| Process                  | Material | Orientation | Temperature (K) | Ultimate Stress (MPa) | Elastic Modulus (GPa) |
|--------------------------|----------|-------------|-----------------|-----------------------|-----------------------|
| Fused Deposition Modeling| N12      | XZ          | (295)           | (46)                  | (1.28)                |
|                          |          |             | 77               | 45.8                  | 5.63                  |
|                          |          | ZX          | (295)           | (38.5)                | (1.14)                |
|                          |          |             | 77               | 30.6                  | 5.02                  |
| ULTEM                    | XZ       |             | (295)           | (69)                  | (2.15)                |
|                          | ZX       |             | 77               | 101                   | 7.48                  |
|                          |          |             | (295)           | (42)                  | (2.27)                |
|                          |          |             | 77               | 39.1                  | 3.60                  |
| Selective Laser Sintering| DF EX    | XY          | (295)           | (48)                  | (1.52)                |
|                          |          |             | 77               | 113                   | 7.37                  |
|                          |          | ZX          | (295)           | a                     | a                     |
|                          |          |             | 77               | a                     | a                     |
|                          |          | XY          | (295)           | (50)                  | (5.73)                |
|                          |          |             | 77               | 78.6                  | 7.64                  |
|                          |          | ZX          | (295)           | (33)                  | (3.0)                 |
|                          |          |             | 77               | 85.3                  | 8.45                  |
|                          |          | XY          | (295)           | (43)                  | (1.59)                |
|                          |          |             | 77               | 65.3                  | 5.25                  |
|                          |          | ZX          | (295)           | a                     | a                     |
|                          |          |             | 77               | a                     | a                     |
|                          |          | XY          | (295)           | (48)                  | (3.38)                |
|                          |          |             | 77               | 95.7                  | 7.26                  |
|                          |          | ZX          | (295)           | a                     | a                     |
|                          |          |             | 77               | a                     | a                     |
|                          |          | XY          | (295)           | (49)                  | (3.82)                |
|                          |          |             | 77               | 87.7                  | 7.01                  |
|                          |          | ZX          | (295)           | (33)                  | (1.95)                |

* A ZX print direction was not available from the manufacturer.

b Samples weren't available for testing.

In general, the ultimate strength of 3D printed polymers increases at 77 K. The ultimate strength of material specimens printed using fused deposition modelling decreased for Nylon-12 in both the XY and Z print directions and decreased for Ultem in the Z print direction. Reduced mechanical properties in the Z print direction may be attributable to weaker inter-layer bond strength between successive layers deposited while printing that are normal to the tensile load. The reduction in ultimate strength for Nylon-12 in the XY print direction, parallel to the tensile load is not clear at this scale of testing and would require assessing the microstructure of FDM plastic to determine the micro-mechanical properties. The average ultimate stress of all materials tested is greater in the XY print direction than in the Z print direction at room temperature. The relationship holds at cryogenic temperature for all materials tested here except for SLS printed Duraform HST, in which the ultimate stress is greater in the Z print direction than it is in the XY print direction. The mean for each print direction is on the standard error bound for the opposite print direction indicating negligible difference in ultimate strength rating between the two orientations.

The mean ultimate stress values for SLS printed plastics (XY orientation) vary between 43 and 50 MPa at room temperature; a range of 7 MPa. At cryogenic temperature, ultimate stress varies between 65 and 113 MPa; a range of 48 MPa that represents a large increase in variability between the plastics at cryogenic temperatures. Duraform HST, glass fiber reinforced Nylon-11 and glass fiber reinforced Nylon-12 are considered fibre reinforced composites by their respective manufacturers. Glass fiber reinforced Nylon-12 is filled with carbon fibers and glass spheres to increase mechanical strength while reducing mass. It is not clear which component of the composite material is responsible for the increase in mechanical strength or why the differences are amplified at cryogenic temperatures.

The modulus of all 3D printed polymers increased at 77 K. At room temperature, the modulus for plastics printed in the XY direction is typically greater than the modulus for plastics printed in the Z direction except for Ultem.
5. Conclusions
Additive manufacturing opens a new pathway for creating complex geometry that would otherwise be too expensive or impossible using traditional manufacturing methods. Devices that operate at cryogenic temperatures and require the low thermal conductivity and high strength of engineering polymers can benefit from the advantages in additive manufacturing. We conducted tensile strength measurements at cryogenic temperatures of currently available engineering plastics that are being used in fused deposition modelling and selective laser sintering manufacturing methods. In general, the strength of the polymers we tested at 77 K that were manufactured using SLS increased in ultimate strength by 35.8% to 175%, while the modulus increased by 29.4% to 228% when compared to room temperature values. The ultimate strength of Duraform EX and Ultem decreased in 3 out of 4 cases by 0.4% to 20.6% while the modulus increased from 58.5% to 341% between room temperature and 77K. The general gains in strength and stiffness indicate 3D printed plastics have potential for use in cryogenic environments, although additional fatigue, shear strength, and notch sensitivity studies should be conducted prior to use in critical applications.

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