Improving PLA-based Material for FDM 3D-Printers Using Minerals
(Principles and Method Development)

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Abstract

A method has been developed to study the performance and suitability of thermoplastic polymeric material for Additive Manufacturing (3D-printing) based on Fused Deposition Modeling (FDM). The method has been used to study the benefits of minerals for PLA-based material (filaments) that are commonly used in FDM 3D-printing. An optimized formulation has been presented that enhances the printing performance and print quality, reduces warpage and curling of the edges, and allows 3D-printed PLA objects to be annealed while maintaining their original shape and dimensions. The annealed PLA objects show significantly improved heat/temperature resistance and can withstand temperatures as high as 120°C.

Introduction

Solid objects having complex shapes may be manufactured by additive manufacturing methods that are also sometimes referred to as 3D printing. The method is used to manufacture objects by placing successive layers of material on themselves to form the final printed object. Fused deposition Modeling (FDM) is a type of additive manufacturing, in which molten thermoplastics material are laid down on each other as a thin strand using a print-head that is controlled by a computer aided design software (CAD). The material will then solidify on the print surface and form the printed object.

While traditionally Acrylonitrile-Butadiene-Styrene (ABS) resin has been used in FDM printers for industrial applications, personal desktop printers started with ABS but gradually shifted to PLA (polylactic acid) due to its green reputation, bio-compostability, pleasant smell as well as low shrinkage and good printability. However, PLA based materials used in FDM printers are far from perfect. Many print defect such as curvature (especially at the corners) and warpage of printed parts are commonly observed, which become more visible as the size of printed parts increase. Printing fine details could also be challenging due to melt run-off affected by temperature and viscosity of the melt. PLA based materials also suffer from weak temperature resistance, which may result in the deformation of printed objects under elevated temperatures experienced during storage and shipping or even during usage, e.g. when the objects are placed under direct sun exposure behind a car windshield screen.

It is also not uncommon to see incomplete print jobs, when FDM printers stop extruding the plastic melt. This would require restarting the entire print job without a guarantee that the next print would be complete. Although equipment design is the primary cause of this problem, consistency and reliability of printing material could also be quite important in eliminating the problem. Overall, improving printability and properties of material used in FDM 3D-printers could significantly help transforming these printers into a common household item such as ink-jet printers.

The objective of this study was to evaluate the applicability and effects of minerals on PLA-based material (also called filament) used in FDM 3D-printing, and to develop an optimized PLA-based material solution primarily for personal desktop printers. However, such material would also be...
suitable for industrial FDM printers, such as those offered by Stratasys and 3D-System, or for the newer Arburg Freeformer.

**Experimental Method**

Initial experimental work was conducted using a few different models of desktop printers to understand their capabilities, limitations, and problems. However, the primary FDM printer used in this study was a model M2 Maker Gear printer (Figure 1) because it provided quite some flexibility in working with a full range of extrusion and print surface temperatures, allowed printing relatively large objects, and provided easy access to printer components for maintenance and troubleshooting purpose. It was equipped with a 25 cm x 20 cm heated glass print surface, whose temperature could be controlled between room temperature (unheated) and over 150°C. Filament extrusion temperature could also be controlled in a broad range including the recommended temperature for PLA, i.e. 180°C-220°C.

Another focus of the initial experimental work was on in-house filament production to allow modifying the material used on the printers. Factors such as extruder temperature profile, melt temperature and pressure, type of die, die hole diameter, strand/filament cooling and extension/winding, measuring and adjusting filament diameter, and the effect of melt viscosity were studied in this phase. Subsequent printing of filament produced in-house revealed that the accuracy and consistency of filament diameter are important factors that affect printability and print quality.

After printer selection and filament production, the focus was shifted to understanding factors affecting printability and print quality using either standard (commercial) PLA filaments or in-house filaments made with unfilled and filled resins. Figure 1 shows Maker Gear M2 printer used in this study along with an in-house filament spool, and Table 1 provides a summary of parameters investigated and materials used in the initial phase of this study. Although the project was focused on PLA material, limited printing activities were conducted with polypropylene and ABS for comparison and to gain insight on factors affecting printability.

![Figure 1. Maker Gear M2 3D-Printer using an in-house mineral-filled filament spool, finished printing the “angled beams” shaped on unheated painters’ blue tape](image)

Figure 1. Maker Gear M2 3D-Printer using an in-house mineral-filled filament spool, finished printing the “angled beams” shaped on unheated painters’ blue tape
Table 1. FDM printing parameters and materials studied

<table>
<thead>
<tr>
<th>FDM Printing Parameters Investigated</th>
<th>Printing Material (Filament) Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>• FDM extrusion temperature</td>
<td>• Commercial PLA filaments</td>
</tr>
<tr>
<td>• Print surface temperature</td>
<td>• In-house PLA filaments made from NatureWorks Ingeo 4043D</td>
</tr>
<tr>
<td>• Print surface material (glass, painters’ blue tape)</td>
<td>• 10% mineral filled PLA</td>
</tr>
<tr>
<td>• Using glue stick on glass print surface</td>
<td>• 20% mineral filled PLA</td>
</tr>
<tr>
<td>• Print appearance as shown by color, texture, and smoothness of print surface</td>
<td>• 30% mineral filled PLA</td>
</tr>
<tr>
<td>• Continuous printing ability to complete print job</td>
<td>• Unfilled and mineral filled PP</td>
</tr>
<tr>
<td></td>
<td>• Unfilled and mineral filled ABS</td>
</tr>
</tbody>
</table>

Since no standard procedure existed for evaluating and comparing 3D-printed material and processes, a focus and outcome of the initial phase of this study was on selecting several basic shapes, which could be used as internal standards for studying and comparing FDM 3D-printed material.

**Method Development**

In order to compare the printability, printing properties, and quality of printed objects, the following four shapes (Figure 2) were selected as internal standards for comparing print materials/filaments for FDM 3D-printers.

1) **Test Tower** is a small cube with a rectangular base measured at 30 mm x 20 mm and a height of 2.5 mm. It is called a tower since its height could be significantly higher, but is limited to 2.5 mm to save printing time. Any additional height would have no effect on printability or print quality of the material. This is a basic shape that is quite easy to print, so it is used as an initial screen to determine if a material could be used for FDM printing.

2) **Flat Bar** is a thin bar with the base dimensions of 190 mm x 20 mm and thickness of 1.7 mm. It is a challenging shape to print by FDM due to its one dimension elongation, which enhances the tendency for warpage and detachment from the print surface. It could be used to indicate the tendency of material for one-dimensional warpage and detachment from print surface.

3) **Test Box** is a relatively large box with the base dimensions of 100 mm x 80 mm, base thickness of 2 mm and wall height of 6 mm. It also is a challenging shape to print since it has a high tendency to warp and detach at the corners. It could be used as a standard to evaluate the warpage and detachment tendency of the materials, including curling and bending of the corners.

4) **Angled Beams** is a challenging but small shape to print. It is used as an internal standard for evaluating temperature resistance of PLA materials, so it is essential that the prints are free from defects. This shape could also be used for visual evaluation and ranking of print quality and accuracy as related to controlling unwanted material drip from print nozzle, because the nozzle moves frequently from one beam to another during printing.

The shape is composed of a set of ten beams (square prisms 4 x 4 x 30 mm) attached at the bottom to a support at different angles. The entire shape is sitting on a thin 5 cm x 5 cm square base. The beams are arranged in order from 10 to 70 degree angles from a vertical position, meaning the 70 degree beam being closest to horizontal position (experiencing the highest load) and the 10 degree beam closest to vertical position (under the lowest loads). All beams are 3 cm in length. “Angled Beams” shape is
available on Makerbot’s Thingiverse website at www.thingiverse.com, more specifically at http://www.thingiverse.com/thing:100934 link, where its CAD design could also be downloaded.

Please note that that a 3D-printer may generate a new slicing pattern each time it prints this shape. The slicing pattern determines detailed path and movements of the print-head and, therefore, the quality and completeness of the print especially for this shape (Angled Beams). So, it is important to check the slicing pattern selected prior to printing and the lack of defects after printing. Defects have often observed at the supporting base of the beams, which is essential to be avoided since the integrity of the support may affect the strength and resistance of the beams at elevated temperatures.

![Shapes selected as Internal standards for evaluating 3D printing: 1) Test Tower, 2) Flat Bar, 3) Text Box, and 4) Angled Beams](image)

*Heat/Temperature Resistance Test*

PLA is a semi-crystalline thermoplastic that is known to have relatively large amorphous phase and low glass transition temperature (Tg) of about 55-65°C. The heat deflection temperature (HDT) of most PLA resins is about the Tg of amorphous PLA. Improving HDT of PLA requires achieving maximum crystalline contents of 33%-37% [2]*, which is neither achievable nor desirable (due to negative impacts on shrinkage and warpage) in FDM 3D-printing process. Following crystallization, further improvement in HDT can be achieved with mineral reinforcement [2-4]. While HDT test is normally conducted under relatively severe load of either 0.45 or 1.82 MPa, typical 3D-printed objects normally do not experience such load levels. In order to study heat/temperature resistance of 3D-printed PLA objects under loads that they typically experience, the following method has been developed and used in this study.

- Print a standard “Angled Beams” object (Figure 2, Shape 4) using FDM 3D-printing, and make sure that it is free from defects (as explained above)

- Preheat a typical laboratory oven to the target test temperature (e.g. 70°C), which is the temperature that printed materials are desired to tolerate
- Place printed “angled beams” objects in the oven for 15 minutes at target temperature
- Remove the objects from the oven, measure the angles of the beams, and compare them with those prior to heat treatment.

**Materials Studied**

A large number of minerals were evaluated in this study primarily for use with PLA filaments. Limited tests were also conducted with ABS and PP for comparison and to understand the principles. Most minerals were tested at two loading levels of 10% and 20% using standard shapes presented in Figure 2. In addition, a proprietary PLA-based formulation was developed during this study (called Formulation-1), whose performance is compared with unfilled PLA as well as 10% or 20% mineral filled PLA in the experimental results presented.

Below is a list of minerals used in this study. Materials that satisfactorily completed printing of standard Shapes 1, 2, and 3 were used for printing “Angled Beams” (Shape 4) to study their heat/temperature resistance.

- Four different talc grades (different particle size, morphology/ore source)
- Two ground calcium carbonate (different particle size)
- Two different micas (Phlogopite and Muscovite)
- Two calcined Kaolin (different particle size)
- Two diatomaceous earth (natural and calcined)
- Two perlites (expanded and unexpanded)
- Rutile TiO₂

**Results and Discussions**

Although 3D printers based on FDM technology have been around for quite a long time, their applications have been limited and technical information and standards defining the technology are scarce in open literature. Therefore, some principles of additive manufacturing using FDM technology are briefly discussed in this section and supported by the experimental data from this study.

**Printability: Detachment from Print Surface**

The primary challenge for completion of a print job is the ability of the extruded plastic strand to stay attached to print surface (bed) during the entire printing process, which could last from a few minutes to many hours. In fact, this very factor is the main reason the thermoplastic resin selection for FDM 3D-printing has been limited primarily to ABS, PLA and a few other resins. Industrial printers have been utilizing many different solutions to address the detachment problem, e.g. using heated print stage, heated print chamber, special anchors or textures on the print stage, etc. For desktop printers used in households or small businesses, however, material selection/modification to enable better attachment to print surface and the completion of print job is a more suitable option.

Most desktop FDM printers use a print stage that is made of glass. Some may be able to utilize a heated print surface, but the simpler models use an unheated print stage. So, an initial objective of the project was to compare the printability of different material on the glass print-stage, and to determine if the printability of PLA on glass could be improved.
A few initial attempts of making polypropylene filaments and using them for FDM printing showed that problems with making the filaments and extruding them with the FDM printers could be rather easily addressed, but extruded PP strands would easily and quickly detach from the print stage even for a small print such as the “Test Tower” (Figure 2). Experimenting with commercial ABS (acrylonitrile Butadiene styrene) and PLA filaments showed much lower detachment tendency, but even these materials had difficulty with attachment to unheated glass.

ABS required elevated print surface temperatures of about 100-110°C to stay attached and complete printing shapes 1, 2, and 3 shown in Figure 2. Attempts to print with ABS on unheated glass or other surfaces were not successful. Some printer manufacturers also provide perforated surfaces to help with anchoring the print object on the print surface, but even these surfaces did not allow printing with ABS without heating the print surface. The best solution was to first print a weak “raft” base on the heated glass, then print the desired shape on the ABS “raft” that could be later broken off from the desired shape.

PLA shows lower tendency to detach from print stage, but even PLA could not be printed sustainably on an unheated glass stage. Our tests show that the best attachment of PLA is obtained when the print surface temperature is increased to 70°C-80°C (slightly higher than the glass transition temperature or softening point of PLA). Alternatively, other options for printing on unheated surfaces are: 1) to cover the glass surface with “blue painters’ tape”, and 2) to apply a glue (such as the typical glue sticks) on the glass surface. Increasing PLA extrusion temperature also helps with attachment to print surface.

As shown in Table 2, PLA can be printed on unheated “painters’ blue tape” at elevated extrusion temperatures (110°C-120°C). However, such temperatures were often too high to print smoothly, causing sudden vapor release (“poofing”) or even yellowing/burning marks especially on humid days. Table 2 shows the results of our FDM printing studies after the addition of 10% or 20% of a wide selection of minerals to PLA at two boundary temperatures of 180°C and 220°C. As seen in

<table>
<thead>
<tr>
<th>Minerals in PLA (Ingeo 4043D)</th>
<th>10% mineral on “Blue Tape”</th>
<th>20% Mineral on “Blue Tape”</th>
<th>20% Mineral on Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (unfilled PLA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talc-1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Talc-2</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Talc-3</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Talc-4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>GCC-1 (ground calcium carbonate)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Mica-1</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>C.Kaolin-1 (calcined kaolin)</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>C.Kaoline-2 (calcined kaolin)</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>DE-1 (diatomaceous earth)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>DE-2 (diatomaceous earth)</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Perlite-1</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Rutile TiO₂</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Formulation-1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 2. Printability data for different minerals and mineral loading on unheated glass and “Painters’ Blue Tape” stages at extrusion temperatures of 180°C and 220°C.
Table 2, the addition of most minerals helps with attachment of PLA filaments to the print surface, especially on “blue painters’ tape”. In this table, materials that are shown to be printable at 220°C but not at 180°C have an optimum print temperature that falls in between these temperatures. Our experience shows that it is best to maintain the printing temperature of PLA below 210°C, which is easily achievable with the addition of quite a number of minerals tested. Some of the minerals tested, increased instability and degradation of PLA despite improving printability so they were not found suitable for the application. Formulation-1 represents a proprietary mineral-filled PLA-based formulation that shows the best print quality while allowing a smooth and sustainable print at temperatures below 200°C.

Limited number of tests conducted with glue stick on unheated glass showed similar or better attachment of PLA based filaments than those on “painters’ blue tape”. So, materials shown in Table 3 to complete printing on “painters’ blue tape” could also print on print surfaces that are covered with glue stick.

**Shrinkage and Contraction**

During FDM printing, thermoplastic polymers (or filled compounds) are laid down as a molten strand or extrudate on the print surface. If the print surface is cooler than the melting or softening temperature of the plastics, the strands would solidify on the surface. The solidification of plastics typically results in a reduction in their volume (shrinkage) followed by further thermal contraction as temperature decreases below their solidification temperature. The net effect of these phenomena is a decrease in size of the printed shape compared to the original dimension that was laid down on the print surface. This could result in warpage, distortion or curling of the edges or base of the printed shape, and in severe cases partial or complete detachment from the print surface.

In FDM 3D-Printing, solidification shrinkage is the main factor contributing to detachment of printed shapes from print surfaces because it happens quite rapidly. In comparison, the effect of thermal contraction is weaker and happens gradually as the plastic temperature decreases after solidification. However, severe thermal contraction may also cause enough dimensional changes and warpage to detach the print job later in FDM printing process. Thermal contraction or expansion is measured as the coefficient of linear thermal expansion (CLTE). Other factors such as interaction with the print surface could also be important.

Amorphous plastics (such as ABS) typically undergo significantly lower shrinkage upon solidification than semi-crystalline plastics (such as PP) due to their unstructured amorphous orientation in solid state. In comparison, semi-crystalline plastics experience more severe shrinkage as they form highly structured crystalline domains during solidification. In addition, the solidification shrinkage happens at a much slower rate in amorphous polymers since they do not have a melting or solidification point. The solidification of these resins starts around their full melting temperature and grows as temperature decreases until full solidification that happens at the glass transition temperature (Tg). As a result, amorphous polymers show much smaller shrinkage upon solidification and expansion/contraction due to temperature change (shown by CLTE). Table 3 compares shrinkage and coefficient of linear thermal expansion (CLTE) of some common semi-crystalline and amorphous polymers.

Although PLA is considered a semi-crystalline resin, it has quite a wide melting range from the softening temperature of its amorphous phase (Tg) at about 60°C to around the melting temperature of crystalline PLA (Tc) at about 150-180°C. It also has a quite a slow crystallization rate, very low shrinkage and moderate to low CLTE (Table 3), which make it quite an ideal material for FDM 3D-Printing. One may note that most amorphous resins shown in Table 3, have been used or could be used for FDM 3D-printing. However, a comparison of CLTE of the
Table 3. Mold Shrinkage (solidification shrinkage) and Coefficient of Linear Thermal Expansion (CLTE) of some common semi-crystalline and amorphous plastics.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Minimum Shrinkage, %</th>
<th>Maximum Shrinkage, %</th>
<th>Minimum CLTE, $10^{-5}/\degree C$</th>
<th>Maximum CLTE, $10^{-5}/\degree C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEKK (Polyetherketoneketone– Low crystallinity)</td>
<td>0.004</td>
<td>0.005</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>PAI (Polyamide-Imide) low friction</td>
<td>0.1</td>
<td>0.5</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>PS (Polystyrene) crystal</td>
<td>0.1</td>
<td>0.7</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>PVC (Polyvinyl Chloride) rigid</td>
<td>0.1</td>
<td>0.6</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>PAN (Polycrylonitrile)</td>
<td>0.2</td>
<td>0.5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>PI (Polyimide)</td>
<td>0.2</td>
<td>1.2</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>PLA (Polylactide-injection molding)</td>
<td>0.3</td>
<td>0.5</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
<td>ABS (Acrylonitrile-Butadiene Styrene)</td>
<td>0.7</td>
<td>1.6</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>PC (Polycarbonate)</td>
<td>0.5</td>
<td>0.7</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>ABS (Acrylonitrile-Butadiene Styrene/Polycarbonate)</td>
<td>0.5</td>
<td>0.7</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>ABS/PC (Acrylonitrile-Butadiene Styrene/Polycarbonate) 20% glass fiber</td>
<td>0.2</td>
<td>0.3</td>
<td>1.8</td>
<td>2</td>
</tr>
<tr>
<td>HDPE (High Density Polyethylene)</td>
<td>1.5</td>
<td>4</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>Polypropylene copolymer</td>
<td>2</td>
<td>3</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>Polypropylene homopolymer</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>17</td>
</tr>
<tr>
<td>Polypropylene 10-40% talc</td>
<td>0.9</td>
<td>1.4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Polypropylene 30-40% glass fiber</td>
<td>0.1</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>0.5</td>
<td>1.5</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>Polyamide 6-6</td>
<td>0.7</td>
<td>3</td>
<td>5</td>
<td>14</td>
</tr>
</tbody>
</table>

Amorphous polymers with that of minerals shows about an order of magnitude lower CLTE for minerals [1]. More importantly, the minerals remain solid in the melt processing of plastics, e.g. during FDM printing, and do not experience any shrinkage. Therefore, the addition of minerals to 3D printing filaments, including PLA based filaments reduces their shrinkage and CLTE; therefore, contribute to improving printability and attachment to print surfaces (as shown in Table 2) and reducing warpage, curling and similar printing defects.

Print Quality: Warpage

Solidification shrinkage and thermal contraction upon cooling could result in curling at the edges and warpage of the base of printed shapes. Print objects with larger base dimensions normally have higher tendencies to warp, which is why we used “Flat Bar” and Test Box” shapes (Shapes 2 and 3 in Figure 2) as two internal standards for studying the warpage and detachment of objects printed using FDM printers. To quantify warpage for these printed shapes, the following definitions/measurements were used:

Flat bar warpage (in mm) is the height of one end of printed bar from a horizontal surface, when the bar is laid flat on the horizontal surface and its other end is pressed and held parallel onto the horizontal surface. The measurement is repeated for both end of the bar and the maximum reading is used as warpage indicator.

Test Box warpage (in mm) is defined as the maximum height measured when test box is laid flat on its base on a horizontal surface, one edge is pressed against and held parallel onto the surface and the height of opposing edge is measured. The measurement is repeated for all edges and the maximum reading is used as warpage indicator.
Figures 3 and 4 show the warpage measured for “flat bar” shape. Commercial neat PLA filament did not complete printing of this shape at 180°C, but did with rather large warpage at 220°C extrusion temperature. The majority of mineral filled PLA filaments did complete printing at both temperatures and showed lower warpage than neat PLA. The large variations (standard
deviation) seen in these results are mostly related to limitations of desktop printer(s) used, inconsistency of material diameter (in-house filaments), and instability of PLA during printing (including some due to the presence of certain minerals). The best printability and lowest warpage in this case belongs to Formulation-1.

Figure 5 shows the warpage measured for “Test Box” specimens printed at 220°C extrusion temperature. Here, many minerals did not improve warpage compared to the unfilled PLA, but some did and Formulation-1 clearly showed the best performance (lowest warpage).

Figures 3-5 show no clear effect of increasing the mineral loading from 10% to 20%. Although increasing mineral loading should theoretically reduce warpage, this was not always the case due to printing and filament instability and sometimes inconsistent feeding of the filaments. In order to obtain the best performance, the mineral selection, mineral loading, and other formulation components have been optimized in a separate study, from which Formulation-1 has been selected to be compared with the basic formulations used in this study.

Figure 6 provides a visual comparison of curling (warpage) observed for ASTM tensile bars printed using standard PLA in comparison with those printed using Formulation-1. While standard PLA shows significant curling on the edge of the print and basically give a defective print, Formulation-1 prints warpage-free (curl-free) on an unheated “blue painters’ tape” surface. Note
that the tensile bars were printed vertically on their longer edge, so the curled edges were in
direct contact with the print surface.

Print Quality: “Relative Weight”

Print quality is an essential requirement for 3D printed shapes, but it is a general term and difficult
to quantify. Many processing factors may contribute to damaging the appearance/quality of the
print, but they all are typically caused by either filament feeding problem (could be machine or
material related), PLA degradation or melt flow issues. Degradation of PLA could occur at
extrusion temperatures exceeding 200°C especially in the presence of moisture or surface active
materials, which typically results in a “cheesy” appearance, emission of vapors at the extrusion
head, dark spots on the print, and run off or dripping of print material at the extrusion nozzle. PLA
degradation, material feeding problems and other factors affecting print quality are very hard to
quantify. We have found that these factors typically affect the extrudate flow at the print-head and
therefore the final weight of the printed shape. Therefore, a parameter was defined that compares
the weight of a printed shape with that of a perfect print. This is called “Relative Weight” (RW), but
it should be corrected for material density if different print materials are compared, which will then
convert to a “Relative Volume” comparison.

\[
\text{"Relative Weight"} = \frac{\text{Weight of printed shape (corrected for material density)}}{\text{Weight of a perfect print (reference)}}
\]

A good print is expected to have a “Relative Weight” (RW) of close to 1 or 100% (±10%). If the
“relative weight” is significantly lower than 100%, the printed object is weak (mechanically and
thermally). On the other hand, excessively high relative weights could indicate low viscosity (high
melt flow), dripping or material run-off, which results in rough print surface and poor appearance.
Printing (extrusion) temperature could be optimized to bring RW closer to 100%.

Figures 7 shows the “Relative Weights” of “Test Boxes” printed at 220°C extrusion temperature,
indicating the range of acceptable quality (±10% variation) by the shaded area. Most printed

Figure 7. “Relative Weight” (RW) of “Test Box” shapes at 220°C extrusion
temperature
objects shown in Figure 7 have acceptable quality, except for 5 prints with high RW and one with low RW. When comparing mechanical or thermal properties of 3D-printed materials, only printed shapes with acceptable RW should be used.

Heat/Temperature Resistance

FDM 3D-printed PLA objects typically soften around glass transition temperature of amorphous PLA (55-65°C), which is undesirable as printed PLA objects may soften and lose their shape or integrity during storage, transportation, or upon extended sun exposure. As described earlier, an internal method has been developed to compare heat/temperature resistance of 3D-printed objects.

Figure 8 shows a comparison of the “angled beams” shapes printed with standard PLA and with a 20% minerals filled PLA compound after 30 minutes of exposure to 70°C temperature. There is a clear deformation in the shape printed with PLA, while the mineral filled compound has primarily maintained its shape. More specifically, the angles of most of the beams have changed significantly for standard PLA. Figure 9 shows the effect of minerals on the angle of 45 degree beam at 10% and 20% mineral loading. The larger the angle of each beam becomes (from vertical position), the worse is the deformation/bending due to temperature. Similar results were obtained using the angle of other beams in the “angled beams” shape (not shown in Figure 9).

Although data presented in Figure 9 show improvement in temperature resistance (shown as smaller angles of the beams) after adding some minerals to PLA, many minerals tested did not show a significant improvement. In addition, significant variations are seen in the data. While the weak performance for some minerals is real and primarily due to their interactions with PLA (during printing), many of weak performances were caused by weak prints resulting from improper slicing pattern (a printer variable) and other printing conditions/parameters.

To address the print deficiencies, “relative weight” (RW) were determined for the “angled beams” shapes used in the oven tests. The results for all talc minerals is shown in Figure 10, indicating a strong effect of “relative weight” (RW) (i.e., print quality or completeness) on the results (angle of 45 degree beams after exposure to 70°C temperature for 30 minutes). The correlation of the results with RW appeared to vary from one mineral to another, which is why other minerals are not included in Figure 10. Since the RW criteria for obtaining the “acceptable” 3D-printed shapes was developed after conducting the tests presented in Figure 9, the data shown in this figure include both “acceptable” and “unacceptable” prints, which is responsible for the large variations.
in results including weak performance shown for some minerals. However, the data points shown for standard PLA and for Formulation-1 are obtained from “acceptable prints” (±10% deviation in RW), and show a clear improvement in heat/temperature resistance of Formulation-1 compared to standard PLA.

Figure 9. Effect of minerals on the angle of 45 degree beam after 30 minute exposure to 70°C temperature

Figure 10. The correlation of “Relative Weight” with the Angle of 45 degree beam after 30 minute exposure to 70°C for all talc samples tested
Annealing of 3D-Printed PLA

It has been shown that weak temperature resistance of PLA could be significantly improved by achieving near maximum crystallization, which is about 35-37% crystalline content [2]. A simple and practical way of achieving maximum crystallinity is by heat treatment (annealing) at temperatures above glass transition (Tg). Annealing temperatures of 70-80°C and the presence of a nucleating agent is typically required to reach maximum crystallization within a reasonable time frame [2]. However, there is a major difficulty with annealing of 3D-printed objects, which is their deformation and loss of integrity (original shape) at annealing temperatures. This happens since PLA softens at annealing temperatures and the load-bearing parts of the object can no longer withstand the weights and forces applied by the other parts of the structure. The “angled beams” shape has been selected for this study because it simulates some of the extreme forces that could be applied on a 3D-printed shape and because it provides means for quantifying the deformation or distortion of its original shape (through angles of the beams).

We have shown that “angled beams” printed using some mineral filled PLA and more specifically using Formulation-1 maintained their shape, while the “angled beams” printed using neat PLA was significantly deformed during annealing (Figure 8). We have further observed that annealed ‘angled beams” shapes could withstand temperatures as high as 120°C after the initial heat treatment test.

Figure 11 shows a comparison of heat/temperature stability of annealed “Formulation-1” with standard PLA. The experiment shown in this figure was conducted by placing five bars of the same dimensions (ASTM flex bars) in an oven whose temperature was increasing from 80°C to 120°C at a rate of 1°C/minute (picture on the left). The bars were positioned horizontally in between two plates, which held the bars in the middle supporting the weight of the other half of each bar. All bars were printed using the same FDM printer and same printing conditions with “acceptable” RW (relative weight). The bar on the left (Figure 11-A) or top (Figure 11-B) was printed using standard PLA, while the other 4 bars were printed using “Formulation-1”, then annealed at 80°C respectively from the left (or top) for 15, 30, 60, and 120 minutes. After a few minutes in the oven, the bar on the left started to gradually bend downward as PLA softened and could no longer support the weight of the hanging half of the bar. The gradual bending of standard PLA bar continued while the oven temperature was increasing, but reached a final bent after some time. The other 4 bars (printed with “Formulation-1”) did not show any bending as seen in both pictures in Figure 11. We did not conduct DSC analysis to determine the crystalline content of each “annealed” bars; however, based on the results of the tests, it could be concluded that significant crystallization was achieved even for annealing time of 15 minutes at 80°C.

Figure 11. Comparing standard PLA (the bar on the left in Pic. A and on the top in Pic. B) with annealed “Formulation-1” (the other 4 bars) after exposure to temperatures escalating from 80 °C to 120°C at a rate of 1 °C/minute.
**Effect of Minerals on PLA Melt Flow Rate**

Melt viscosity or melt flow rate is a significant factor in material selection for FDM 3D printing, which may vary with the type of resin or compound used. The common PLA resin used as the commercial filament material for FDM 3D-printing is Ingeo 4043D from Nature Works. The same resin has been used as the base material for all formulations in this study. Figure 12 shows the melt flow rate (MFR) of this resin as well as a number of 10% and 20% mineral filled Ingeo 4043D formulations measured at 10 kg force as a function of temperature. Data shows that adding 10% minerals had a small decreasing effect on melt flow of PLA, but the effect was reversed at 20%. Overall the effect of minerals tested on melt flow of PLA was found to be too small to impact extrusion of PLA in FDM 3D-printers.

Data presented in Figure 12 clearly shows that elevated temperatures (e.g. 240°C) could significantly increase PLA melt flow (likely due to excessive PLA degradation). For the best print quality, the extrusion temperature needs to be optimized for any new material used for FDM 3D-Printing (including mineral filled PLA).

![Figure 12. Effect of mineral loading and temperature on melt flow rate (MFR) of Ingeo 4043D PLA](image)

**Material Selection**

In addition to printability and print quality discussed above, a number of other parameters influence the selection of a PLA-based material for 3D-printing. These include factors affecting the production of filaments needed for printing, mechanical properties of the material (printed objects), and factors affecting feeding and extrusion of the filaments at the printers. Filament feeding problems, for example, could be a major concern for the users as hours of printing could be wasted when a print job cannot be completed. Feeding problems could happen due to:

- breakage of the filament,
- excessive hardness of the filament surface causing insufficient grip at the feeding gear,
- excessive heat and softness of filaments at the feeding gear,
Following the study presented in this paper, a material optimization study was conducted for the selection of mineral-filled PLA-based material for FDM 3D-printing, which could be the subject of a separate publication. "Formulation-1" is one of the materials from that optimization study, which was selected to be softer than standard PLA to reduce filament feeding problems caused by filament breakage and insufficient grip at feeding gear. It has similar melt flow to standard PLA and could be 3D-printed on an unheated stage (preferably covered with "blue painter's tape") at the recommended extrusion temperatures of 180-200°C.

As shown in Figure 13, the stiffness (flexural modulus) of "Formulation-1" falls in between standard PLA and ABS that are the two most common materials used for desktop FDM 3D-printing. Figure 14 shows that the notched IZOD impact resistance of "Formulation-1" also falls in the range between standard PLA and ABS, but the un-notched IZOD impact is superior than both ABS and standard PLA. After annealing the un-notched IZOD impact of "Formulation-1" is further improved and achieves "non-break" status based on ASTM D790 definition.

In addition to the improved temperature resistance shown in Figures 9 and 11, annealed "Formulation-1" showed a higher HDT (at 64 psi load) than standard PLA (Figure 15) despite being softer than PLA (Figure 13). This implies achieving quite high crystalline content during annealing. Annealed "Formulation-1" could eliminate the temperature resistance difficulties that 3D-printed PLA objects suffer from during storage or upon extended exposure to sun beams.
Conclusions

A method has been developed to evaluate thermoplastics materials for use in FDM 3D-printers. It provides means for evaluating the attachment of extruded materials to print stage (completing the print job); to compare warpage, curling and deformation of printed objects; to compare the overall consistency and quality of the printed objects; and to evaluate the temperature/heat resistance of PLA based material which may soften and deform during application or storage/transportation. The method was used to investigate benefits of mineral-filled PLA by comparing with typical PLA filaments used for desktop FDM 3D-printing.

The results show that the addition of some minerals to PLA does improve the attachment of print material to the print stage, and allows printing at lower extrusion temperatures and on unheated print stages including on glass and on “blue painters’ tape”. The addition of minerals could also reduce shrinkage and improve the quality of print jobs by reducing warpage and curling of the edges. It is also observed that the addition of some minerals, such as talc, could improve the temperature resistance of PLA.

“Formulations-1” is a proprietary mineral-filled PLA formulation developed based on the results of this study, whose improved processing and printability, as well as lower warpage, curling and better print quality has been presented along-side the mineral filled PLA data in this paper. “Formulation-1” is shown to allow printed objects to be annealed at 70°-80°C without losing their shape and integrity. Following annealing, printed objects from “Formulation-1” could withstand temperatures as high as 120°C. “Formulation-1” is selected to be softer than PLA to minimize filament breakage and flexibility issues. Its stiffness (flexural modulus) and notched IZOD impact strength fall in between standard PLA and ABS that are commonly used for FDM 3D-printing. However, it shows enhanced HDT and “no break” performance in un-notched IZOD impact test after annealing.

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