Preparation and characterization of a newly developed polyamide composite utilising an affordable 3D printer

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Abstract
In this work, the potential of polyamide composite prepared by a 3D printer was evaluated. Polyamide 12 was compounded with 5 wt% hydroxyapatite and 15 wt% zirconium oxide fillers via a twin screw extruder. The compound was then pelletized prior to the preparation of the filament by a desktop filament extruder. The filament was finally applied to a 3D printer to prepare the printed tensile samples. Pure polyamide 12 and commercial polyamide filament, Taulman 618, were also printed and tested for control. Melt flow and thermal analysis were carried out to estimate the processing conditions. Tensile test was also conducted to evaluate the strength and modulus. The new polyamide composite was successfully prepared and tested. The strength of polyamide composite was comparable to Taulman 618. The modulus of the composite was improved due to the incorporation of fillers. The morphology of the printed composite was porous, which could provide pros and cons to biological and mechanical properties, respectively. Polyamide composite presented a promising polymer material for a 3D printer and may be applied for biomaterial application.

Keywords
Three-dimensional printer, RepRap, filament extruder, polyamide

Introduction
Over the past several years, the demand for affordable, hobbyist three-dimensional (3D) polymer-based printer was incredibly high due to the revolution of the RepRap (replicating rapid prototype); the first open-source, self-replicating rapid prototype. Although still in infancy, 3D printers are rapidly maturing, which apparently signifies unlimited potential in various applications. According to the report by the Freedonia Group, the demand for 3D printing is estimated to rise more than 20% per year so as to reach $5 billion in 2017.¹ With its capability to manufacture 3D objects, it is expected to be utilised in the manufacturing of direct production parts and finished goods.

Adopting from Fused Deposition Modelling (FDM) technology, created by Stratasys Corporation, the hobbyist 3D printer is getting more attention from crowds due to its low cost and unlimited material that may tried within the printer’s specification. There are a large number of companies selling hobbyist 3D printers at the market, such as Makerbot, Ultimaker, Solidoodle and others, which greatly offer lower prices in comparison to professional 3D printers. While most professional 3D printers cost at least $50,000, hobbyist 3D printers only cost between $500 and $3000, depending on the size of build, print resolution, temperature of extruding and printer's accessories.² The high demand for 3D printers also

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resulted in the invention of the desktop filament extruder. By using a desktop filament extruder, the cost of materials will be significantly reduced; and at the same time, users can also try new materials, or modify any potential material, to be utilised for 3D printing. However, in order to be compatible with a 3D printer, the material used (which is in filament form) should be in a specific diameter range; from 1.65 to 1.85 mm. It should also possess equal or higher flowability compared to commercial filaments in the market, such as acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA), in which the 3D printer has been optimised.

Another important field in 3D printing is the development of materials used as the ‘ink’ in 3D printers. Two types of widely used polymer materials in 3D printing are PLA, an environmentally friendly material derived from corn starch, and ABS, a polymer derived from fossil fuels. Polyamide (PA) is a new, alternative material for 3D printing and receives plenty of attention from users due to its desirable properties in comparison to common ABS and PLA. According to Taulman,3 PA shows almost no delamination in which the bonding strength of thread-to-thread is comparatively higher than ABS or PLA, even though the parts have been subjected to split at right angle transitions.

PA is one of the most commonly used polymers in biomedical applications. PA exhibits good biocompatibility with human tissues, enhanced mechanical properties (particularly high toughness), excellent sliding and wear characteristics and is also chemically stable. In recent years, bio-ceramic fillers such as hydroxyapatite (HA), β-tricalcium phosphate (β-TCP) and bioactive glass have been incorporated in polymers to enhance the bioactivity of materials that induce the formation of an apatite layer on surfaces. A recent study by Afzal4 also described the potential usage of zirconium oxide (ZrO2) in orthopaedic application due to its unique biomechanical properties including mechanical strength, fracture toughness, biocompatibility and bioactivity. Until this day, different approaches have been employed to explore the potential of PA composite for scaffolds, implants and orthopaedic applications using conventional techniques such as injection moulding, compression, solvent casting, co-solution method and infiltration of polymers.5–10 Despite the fact that 3D printing is recognised worldwide, no study was reported regarding the preparation of PA composite via 3D printing.

Thus, a systematic study on the experimental condition of 3D printed PA composite was necessary for providing a new method to fabricate a biomedical device in a rapid and convenient manner. This research can also be a good preliminary study for further development in 3D printing technology, and the product obtained could potentially be used as a material for sustainable development in biomedical applications and other areas. This study focused on fabricating a PA reinforced with ZrO2 and HA utilising an affordable hobbyist 3D printer. Melt flow and thermal analysis were carried out to estimate the processing conditions. Finally, mechanical properties were evaluated and compared with commercial PA.

**Experimental**

**Materials**

The FDA approved PA 12 (PA 2200), supplied by EOS GmbH, was used in this study. ZrO2 (AC19052-2500) and HA (21223) were purchased from Acros Organics and Sigma-Aldrich, respectively. The purity of ZrO2 was 98.5%, whereas the purity for HA was ≥90%. A commercial PA filament, Taulman 618 with filament diameter of 1.75 mm, was supplied by Taulman, USA.

**Desktop filament extruder setup and operation**

A desktop filament extruder (Extruder Version 1.3, Filastruder) and a winder were bought by kits and assembled according to the manual’s instructions.11 The extruder was mounted vertically on the wall, attached with a winder and a sensor that were placed on the table (Figure 1). The winder was used to spool the filament as it extrudes, using a sensor to adjust the winding speed, matching with extrusion rates, as well as, running it through some PTFE tube to gently coil it as it moves along. By using the winder, the filament would follow a steady, unchanging path from the extruder to the winder, which resulted in better quality filament with a consistent diameter.

**Preparation of PA composite**

**Compounding.** For this particular application, the consideration of the right filler amount of composite was crucial so that no issues will arise regarding its processability and extrudability during printing. High filler content was not recommended as it may harm the 3D printer. Therefore, 20 wt% of fillers were selected; whereby 15 wt% of ZrO2 was chosen according to a study by Sarwar et al.12 which showed the excellent mechanical properties of PA composite at this filler percentage. Meanwhile, 5 wt% of HA was selected as it displayed no waviness occurrence of extrudate during the filament extrusion process. Prior to processing, PA and fillers were dried in the oven at 80°C for 24 h. PA 12 was compounded with ZrO2 and HA fillers (Table 1) in a co-rotating twin screw extruder (PSM 30, Sino Alloy Machinery). PA and fillers were first
dry-mixed by shaking in a plastic bag for 5 min prior to feeding into the hopper. The temperature profiles in the barrel were set at 180–200°C from the hopper to the die, with screw rotating speed of 150 r/min. The extruded strands were immediately quenched after extrusion in a water bath, and were then pelletized.

Fabrication of composite filament. A desktop single screw extruder (Extruder Version 1.3, Filastruder) was used to fabricate the filament from the composite mixture. The pellet was dried in the oven at 80°C for 24 h. The nozzle temperature was set at 185°C until 1.75 mm of filament was obtained. The filament was spooled to the winder as it extruded.

Preparation of 3D parts test specimens. A 3D model was printed via a desktop 3D printer (Replicator 2X, Makerbot) by applying the 1.75 mm fabricated filament (Figure 2). Basically, two common diameters of plastic filaments are 1.75 and 3 mm. Each extruder is designed to work with a specific filament diameter. In this study, 1.75 mm filament was selected since a smaller diameter is capable of being heated in a short period of time and, therefore, the printing process can be quickly accomplished. The virtual 3D model of tensile specimens was constructed via SolidWorks 3D Computer Aided Design (CAD) software. STL file format was then generated to represent the digital model. The next step was to convert the digital model (Figure 3) into a list of commands that the 3D printer could understand and execute, usually known as G-code or slicing. In Makerbot 3D printer, Makerware program was used to slice the 3D model. Setting parameters in Makerware were shown in Table 2. After the G-code was created, it was sent to the printer through a USB connection. A 3D model was printed at the printing platform, layer by layer. Blue painter’s tape was applied as a surface platform to print PA.

Characterisation techniques

Density. The density of PA pellets was measured by using a pycnometer (Accu Pyc 1330, Micromeritics). The mass of pellets was measured before being inserted into a 10 cm³ cavity and placed into the measurement chamber to measure the density. Three measurements were carried out and the average value was taken as the result.

Melt flow index (MFI) value. The MFI of PA was measured by the MFI tester (Dynisco, Polymer Test). For this experiment, 1.2 kg static mass was used to force the PA to extrude through the standard orifice at a melt temperature of 230°C for 360 s. A small portion of five extrudates was cut using a razor blade after 20 s. The mass of extrudates were measured, and the MFI value was determined.

Differential scanning calorimetry (DSC). Thermal properties of PAs were characterised by using a differential scanning calorimeter (Heat Flux Pyris 6, Perkin-Elmer). The specimens were dried at 80°C for 24 h to eliminate the humidity from the samples prior to the test. The specimen’s mass of 10 mg was cut and placed on the calorimeter's sample pan. The calorimeter was then heated at a rate of 10°C/min from 30°C to 200°C. The data was collected and the glass transition temperature, Tg, and the crystallisation temperature, Tc, were determined.
Figure 2. A schematic diagram of fused filament extrusion process.

Figure 3. Tensile test specimen in accordance with ASTM D638 Type 1.
an aluminium pan. The specimen was heated from room temperature to 300°C and then cooled to 0°C at a heating rate of 10°C/min under nitrogen atmosphere. The melting point \( (T_m) \) and recrystallization temperature \( (T_c) \) were obtained from the DSC curves.

**Thermogravimetric analysis (TGA)**. TGA (Pyris 6, Perkin-Elmer) was performed in nitrogen atmosphere from room temperature to 600°C at a heating rate of 10°C/min. The thermal decomposition temperatures as well as the filler contents in the composites were determined from the TGA curves.

**Filament diameter**. The diameter of the produced filament was measured at several places by a micrometre. At least 30 measurements were accomplished out of 15 m filament.

**Mechanical properties**. Strength and modulus of specimens were measured using a universal testing machine (Model 3366, Instron), fitted with a 10 kN load cell and at a crosshead speed of 5 mm/min. The specimen dimension followed ASTM D638 Type 1. The strain gauge was set at 80 mm. Five specimens were tested and the average value was taken as the result.

**Field emission scanning electron microscopy (FESEM)**. The morphology of the fractured surface of tensile and cryofractured specimens was examined by FESEM (Supra 35 VP, Carl Zeiss) after the specimens were sputtered with aurum alloys.

### Results and discussion

#### Melt flow properties

The MFI was measured to determine the capability of PA to be fabricated through a desktop filament extruder. In this study, a desktop filament extruder was used to fabricate the PA filament. Here, it should be clarified that the machine was only for lab scale purposes and not recommended for industry use. Although the size of the extruder was small, it was compatible to a single screw industrial extruder. One of the main differences would be the screw type, in which an industrial extruder has a tapered centre section to increase shear and compression, while a desktop extruder has a constant cross-sectional area that reduces the capability of a machine to operate at low pressure (~150 lbf/in²) and low temperature (~200°C). As this extruder was optimised to fabricate ABS filament, the material with lower MFI than ABS is not recommended to be used for filament fabrication. This filament extruder can support polymer that has MFI value equal to or higher than 11 g/10 min (230°C/3.8 kg load). Polymers that show high viscosity or low MFI require greater torque and increased motor load. PA primarily exhibits high viscosity than ABS; therefore, it can be fed to the desktop extruder. From the obtained results (Table 3), although the incorporation of fillers significantly lowered the MFI value of PA, this value was still higher than ABS. The presence of fillers may interrupt the segmental motion of the polymer, thereby, reducing the chain mobility and lowering the MFI values (increase melt viscosity). This, in turn, may affect the morphology of the composite, which was later discussed.

#### Thermal properties

To appropriately compare the properties of pure PA and composite, it was necessary to fabricate these materials under the same processing conditions. The thermal properties of PA and composite were determined by DSC and TGA. Table 4 provided a summary of the results. The melting temperature of PA12/ZrO₂/HA composite was 180.7°C, while unfilled PA was 181.5°C. The presence of fillers slightly lowered the melting temperature \( (T_m) \) of the composite than the pure PA. Incorporation of fillers may destroy the crystal perfection which forms smaller crystallite than one found in pure PA. The reduction of crystallite size increases the surface-to-volume ratio of the crystallites,
resulting in a higher interfacial free energy, hence, lowering the melting point ($T_m$) for the crystalline phase.\textsuperscript{14} The increase in the crystallisation temperature ($T_c$) of the PA composite compared to that of the unfilled PA clearly indicated the role of fillers as a nucleating agent. This occurrence, known as heterogeneous nucleation, specifies that the crystallisation rate can be improved if the nucleating agent is added to the system.\textsuperscript{14} It was reported that many studies\textsuperscript{5,9,15,16} also found the same pattern as the present study.

The processing temperature was set at 180–200°C and 185°C via a twin screw extruder and a filament extruder, respectively. These temperature settings were only slightly higher than the melting temperature of the materials, which is a common practice in determining the processing temperature. Nevertheless, the printing temperature was set a bit higher, at 230°C. In fact, PA can be extruded down to as low as 190°C. However, the thread bonding of layered parts was not sufficient at temperatures below 230°C. From DSC and TGA results, PA displayed wide processing windows (temperature range from melting to decomposition), therefore, a printing temperature at 230°C was still acceptable.

According to the TGA results in Table 4, PA12/ZrO$_2$/HA composite exhibited higher stability than unfilled PA. Unfilled PA underwent thermal degradation beginning at 422.48°C, whereas, the composite started to decompose at 437.7°C. The improved thermal stability of PA/ZrO$_2$/HA composite may be due to higher thermal stability of ZrO$_2$ and HA fillers. The manufacturing of PA requires the mixing of fillers and matrix at high temperatures, therefore, the degradation of PA can produce undesirable effects on the end properties if the material is heated at the temperature close to the degradation point. The manufacturing was conducted at the temperature range of 180–230°C, which was still far below the point of degradation temperatures.

Figure 4 presented the effect of filler content on thermal stability of PA12/ZrO$_2$/HA composite. A mass loss of 78.14 wt\% occurred, which corresponded to a matrix content in the composite; while 21.86 wt\% of residue

\begin{table}[h]
\centering
\caption{Thermal properties of polyamides.}
\begin{tabular}{lllll}
\hline
Material & Filler (wt\%) & $T_m^a$ (°C) & $T_c^b$ (°C) & $T_d^c$ (°C) \\
\hline
Unfilled PA12 & 0 & 181.57 & 140.15 & 422.48 \\
PA12/ZrO$_2$/HA & 20 & 180.73 & 143.85 & 437.70 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Melting temperature from DSC first heating at 10°C/min.
\textsuperscript{b}Crystallization temperature measured on cooling at 10°C/min.
\textsuperscript{c}Decomposition temperature determined by TGA at 10°C/min.
\textsuperscript{d}Actual filler content is 21.86\% by weight.

Figure 4. TGA curves of unfilled PA 12 and PA/ZrO$_2$/HA composite, at a heating rate of 10°C/min.
was associated with inorganic fillers. The residual mass recorded by TGA analysis was comparable to the amount of filler used in the composite (20 wt%) and, therefore, it was presumed that the compounding via a twin screw extruder was able to provide fillers with good dispersion and was well-mixed in the PA matrix.

Filament diameter

High quality of filament is very crucial in obtaining a good 3D printing. Ideally, constant 1.75 filament diameter was preferred across the entire spool. However, due to the manufacturing process, there is always a tolerance in which the diameter will be maintained. Usually, in a 3D printer, 1.75 mm filament features a diameter tolerance of ±0.1 mm. According to the obtained results (Figure 5), both filaments produced were in the range between 1.65 and 1.85 mm, therefore, complying with the required diameter tolerance. Hence, it can be said that the desktop filament extruder was capable of extruding PA with a consistent diameter. The range of composite filament diameter was smaller than unfilled PA12. This was attributed to the incorporation of fillers, which had strengthened the filament profile coming out from the nozzle.

Serious issues can arise from filament diameter out of the allowed tolerance. A decrease in filament diameter could bring about the failure of an extruder due to insufficient pressure gripping on the thin filament, which may finally hinder the plastic flow to the nozzle. On the other hand, if the filament is too wide, the motor would be unable to push the filament through or it may not fit into the nozzle opening. The extruder gear may also shred the surface of the plastic, leaving nothing to grip and finally stalling the extruder.17

Mechanical properties

The printed tensile specimens were successfully fabricated via a 3D printer by applying 1.75 mm filament, as shown in Figure 6. The parts were printed at 100% infill in 0°, 90°, 45° and −45° orientations, alternately, until the process was completed. From the obtained results (Table 5), the strength of PA12/ZrO2/HA composite was slightly lower compared to the unfilled PA, yet showed similar strength to the commercial PA, Taulman 618. The low strength of the composite was mainly due to the formation of porosity, which acted as a stress concentration factor, reducing the strength. The stress–strain behaviour (Figure 7) demonstrated that all materials underwent plastic deformation before failure. PA/ZrO2/HA composite showed the highest modulus but the lowest tensile strain. Incorporation of fillers also made PA more brittle and exhibited less plastic deformation. In comparison to the current materials for biomaterial application, such as polycaprolactone (PCL) and polyethylene glycol (PEG), PA 12 composite presented higher tensile strength and elastic modulus.18,19

Formation of porosity has an obvious effect on mechanical properties. The stresses might concentrate at the weaker interfaces of porous structures. Although PA is classified as a hygroscopic polymer, which tends

![Figure 5. Filament diameter of unfilled PA12 and PA12/ZrO2/HA.](image-url)
to absorb moisture from the surrounding atmosphere, pure PA did not show any porosity on the surface of printed PA (Figures 8(a) and 9(a)). The porosity was only observed after the incorporation of fillers. It was presumed that the porosity was formed during processing through a porous and very fine filler, which absorbed moisture from the environment. In this case, HA that contains a hydroxyl group can be a site for moisture to interact, forming a hydrogen bond in the structure. In an extruder, this moisture turns to steam and produces extrudate, containing bubbles in the material's thread. Although care has been taken by drying the materials for at least 24 h, the problem still occurred. Another assumption was due to the insufficient pressure during printing, which was controlled by speed while extruding. In this study, the parameters set in Makerware program were similar to printing the ABS, except for nozzle and platform temperatures. PA/ZrO₂/HA composite, which showed lower MFI (higher viscosity), may need higher pressure to increase the extrusion rate; thereby, plastic can flow sufficiently and efficiently, producing parts with less void or porosity. It may also be possible that the incorporation of fillers will cause an additional increase in viscosity. It is recommended to increase the speed while extruding, along with the nozzle temperature, to obtain a good flow composite in a 3D printer. Although porosity is not desirable during processing, the porous structure could provide a good support for the bone in growth, and strengthen the mechanical connection between the PA composite and the bone.²⁰

Compared to conventional polymer processing, such as injection moulding, 3D printing technique produces parts with lower strength and modulus of elasticity.¹⁶,²¹

The 3D printed part is built in layers, which means it has laminate weaknesses; especially when the layers do not bond very well in the z-axis. Unlike the injection moulding technique, it consists of high pressure to inject the polymer into a mould, which produces parts with relatively consistent material structure, less voids and porosity; and exhibits excellent mechanical properties across the parts. However, the parts fabricated by injection moulding cannot be customised, and are only useful for large scale manufacturing due to the costs of expensive tooling, moulds or dies. In fact, each technique has its pros and cons that are useful for different applications. Some parameters on desktop 3D printing may also be integrated to enhance the mechanical properties in future work.

**FESEM observation**

FESEM micrographs of fractured surfaces were shown in Figures 8 and 9. Multiple layers of PA were produced after printing. It demonstrated that the thread diameters of unfilled PA of tensile specimen (Figure 8(a)) became smaller compared to the cryofractured sample (Figure 9(a)) due to the elongation of thread structures during the test; leaving air gaps between the threads. The elongated thread and a reduction in the cross-sectional area of PA 12 indicated that this material undergoes large plastic deformation. This resulted in a necking phase of the material, in which polymer chains slip over each other; rearranging the macromolecular structure until fractured. Incorporation of fillers has limits, and it inhibits the sliding of polymer chains past each other; therefore, PA 12/ZrO₂/HA composite tends to break earlier. As previously mentioned, Figure 8(b) depicted a porous surface of PA/ZrO₂/HA composite which can become a site for stress concentration and lower the strength of

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**Table 5. Mechanical properties of polyamides.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled PA12</td>
<td>26.54 (4.12)</td>
<td>644.44 (44.98)</td>
</tr>
<tr>
<td>PA12/ZrO₂/HA</td>
<td>22.78 (3.94)</td>
<td>761.93 (45.99)</td>
</tr>
<tr>
<td>Taulman 618</td>
<td>21.49 (0.31)</td>
<td>429.43 (23.47)</td>
</tr>
</tbody>
</table>

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Figure 6. The a) filament and b) printed tensile specimen after fabricated through filament extruder and 3D printer, respectively.
the material. No elongation of thread structure was observed and the diameters of threads were almost similar prior (Figure 8(b)) and after (Figure 9(b)) the test; corresponding to a brittle fracture. Commercial PA, Taulman 618 (Figure 8(c)) exhibited ductile deformation in which more subtle fibrils were observed on the fractured surface. The thread size of Taulman 618 was bigger compared to the unfilled PA 12, which demonstrated that the sample underwent less plastic deformation. These micrographs supported, and were
in agreement, with the results that had been previously discussed.

Conclusion

A new composite PA material filled with 20 wt% ZrO$_2$ and HA was successfully developed and fabricated via an affordable hobbyist 3D printer to produce 3D parts. The presence of fillers increased the viscosity, rate of crystallisation and thermal stability of the polymer composite. The strength of the composite was comparable to the commercial PA, Taulman 618, with improved elastic modulus. Although the acquired mechanical properties were weaker than those obtained in injection moulding, they were higher and comparable to the current printed materials used for biomaterial applications. Despite several limitations, this preliminary study is an important first step to explore the potential of manufacturing PA composite via 3D printing; and simultaneously, many improvements can be made for future works.

Declaration of Conflicting Interests

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