Jurnal Teknologi

Full Paper

MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLYAMIDE 12 COMPOSITE FOR POTENTIAL BIOMEDICAL IMPLANT: INJECTION MOLDING AND DESKTOP 3D PRINTER

Article history
Received
31 January 2015
Received in revised form
30 April 2015
Accepted
31 May 2015

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Graphical abstract

Abstract

Fused filament fabrication is a filament based rapid prototyping process, which offers the possibility of new polymer material for invention of biomedical implant. This study represents an investigation on a preparation and characterization of new polyamide 12 reinforced with 20 wt% of zirconium dioxide and hydroxyapatite by desktop 3D printer in comparison with conventional manufacturing method, injection molding. Polyamide 12 composite was compounded, pelletized and filament-extruded prior to apply to a 3D printer. Sample prototypes from the new polyamide composite have been successfully made and tested. Mechanical (flexural and impact) and morphological properties were evaluated and compared. From the results, the printed polyamide composite exhibited lower mechanical properties than injection molded due to the formation of porosity, laminate weakness and low pressure during printing. Although the mechanical properties of printed parts were lower than molded parts, but the capability of 3D printer to fabricate any customized 3D object could lead to the bright future and great contribution in this area, while at the same time many improvements can be made for the future works.

Keywords: 3D printer, injection molding, polyamide, hydroxyapatite, zirconium dioxide, implant

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1.0 INTRODUCTION

There is necessity for replacing bone substance which has been lost due to traumatic injuries and non traumatic events. Various materials have been used to fill the defect, however titanium and polymeric materials such as polymethyl methacrylate (PMMA) and polyetheretherketone (PEEK) are the most preferred by surgeons. Recently, 3D printing technology have shown to be an attractive technique to produce biomedical implant compared with conventional intraoperative molding [1] which can improve the aesthetic outcomes, decreases surgical time, blood loss and the risk of infection.

In the past, the cost of 3D printing was expensive and the technology was only used by large corporations, however the development of a desktop, open source 3D printer has made the technology more accessible to anyone with affordable prices. The technique namely fused filament fabrication was adopted from Fused Deposition Modelling (FDM) technology, a prominent form of rapid prototyping created by Stratasys Corporation. Previously many common products such as spare parts for cars and appliances, cell phone cases, and souvenirs have been created, but recently this technology has move forward on developing of more advance tools in various areas including in healthcare. With its capability to produce 3D objects and complicated part designs, 3D printing is becoming more common among surgeons and medical researchers. Currently, it has most success with prosthetics [2], organ model [3], human tissue [4] and medical device [5] which were tailored according to a specific patient. However, the application of this technology to produce the biomedical implant was still unexplored yet.

Accordingly, this study aimed to produce the implant material as a substitution of the hard tissue. Polyamide (PA) was chosen due to its good biocompatibility with human tissue and exhibits good mechanical properties [6]. Zirconium dioxide and hydroxyapatite were used as fillers to enhance the biological and mechanical properties. Mechanical and morphological properties of printed prototypes were evaluated and compared with injection molded specimens.

2.0 EXPERIMENTAL SET-UP

2.1 Materials

The FDA approved polyamide 12 (PA 2200) supplied by EOS GmbH was used in this study. Zirconium dioxide (AC19052-2500) and hydroxyapatite (21223) were purchased from Acros Organics and Sigma-Aldrich, respectively. The purity of zirconium oxide (ZrO_2) was 98.5 %, whereas the purity for hydroxyapatite (HA) was ≥90 %.

2.2 Preparation of Polyamide Composites

Polyamide 12 was compounded with 20 wt% filler loading of zirconium dioxide (ZrO_2) and hydroxyapatite (HA) fillers in a co-rotating twin screw extruder (PSM 30, Sino Alloy Machinery) at barrel temperature of 180-200 °C. Before compounding, polyamide and fillers were dried in the oven at 80 °C for 24 h. The extruded strands were quenched immediately in a water bath prior to pelletizing. The second process was to fabricate a filament with a diameter of 1.75$\pm$0.1 mm through a desktop filament extruder. The nozzle temperature was set at 185$\pm$5 °C and the filament obtained was spooled to the winder during it extrudes. After this process, the filament was finally applied to a desktop 3D printer (Makerbot 2X). The virtual 3D models of tensile and impact specimens were firstly constructed through SolidWorks 3D Computer Aided Design (CAD) software prior to generating of STL file format. This file was then converted into a list of commands that 3D printer could understand and execute, known as slicing. In this study, Makerware program was used to slice the 3D model and sent to the printer through USB connection. A 3D model was printed at the printing platform layer by layer. Painting tape was used as a surface platform to print polyamide. The processing parameters for 3D printer were shown in Table 1. The specimens for mechanical testing were also prepared via injection molding machine as for comparison. The barrel temperature was set at 180 to 230°C from feed to nozzle.

Table 1 Setting parameter in Makerware program

Resolution	standard
Infill	100 %
Number of shells	2
Layer of height	0.2 mm
Pattern orientation	0°, 90°, 45° & -45°
Speed while extruding	90 mm/s
Speed while traveling	150 mm/s
Nozzle temperature	230 °C
Platform temperature	110 °C

2.3 Characterization Techniques

The tensile (ASTM D638) properties of polyamide were characterized using universal testing machine (Model 3366, Instron) at a test speed of 5 mm/min. The impact strength (ASTM D256) of notched specimens was determined using an Izod pendulum tester (Model 5101, Zwick). Five specimens were prepared for each test. Fractured surface of tensile specimens were used to study the morphology by field emission scanning electron microscopy (Supra 35 VP, Carl Zeiss).

3.0 RESULTS AND DISCUSSION

3.1 Fabrication Of PA Composites By Desktop 3D Printer

The printed tensile and impact specimens were successfully fabricated via a 3D printer by applying 1.75 mm filament as shown in Figure 1. The specimens were printed 100 % infill in 0, 90, 45, -45° orientations alternately until the process was completed. The parameters set in Makerware program were used without any modification of initial setting by manufacturer except for platform temperature and nozzle temperature. In the initial stages of processing polyamide, there were several problems related with printing temperature, material warping and clogging. The problems were overcome by increasing the temperature and trying several types of surface platform including kapton tape, paper, hard paper, phenolic cotton laminated plastics, blue painting tape and ABS raft.

Figure 1 Printed tensile specimen fabricated via desktop 3D printer

3.2 Mechanical Properties

The mechanical properties of polyamide (PA) prepared by 3D printer and injection molding are shown in Figure 2. For injection molded PA, incorporation of fillers shows the increase in tensile strength and modulus. These reinforcing filler particles may provide a good filler-matrix interaction, which enable more stress to be transferred from matrix to the filler during external loading. Meanwhile, the strength of printed PA composite shows a slight reduction compared with printed unfilled PA. This can be attributed by the formation of porosity or void at the thread which can be a place for stress concentration, thereby polymer tends to break earlier. According to results of impact strength, the same trend as tensile properties can be observed.

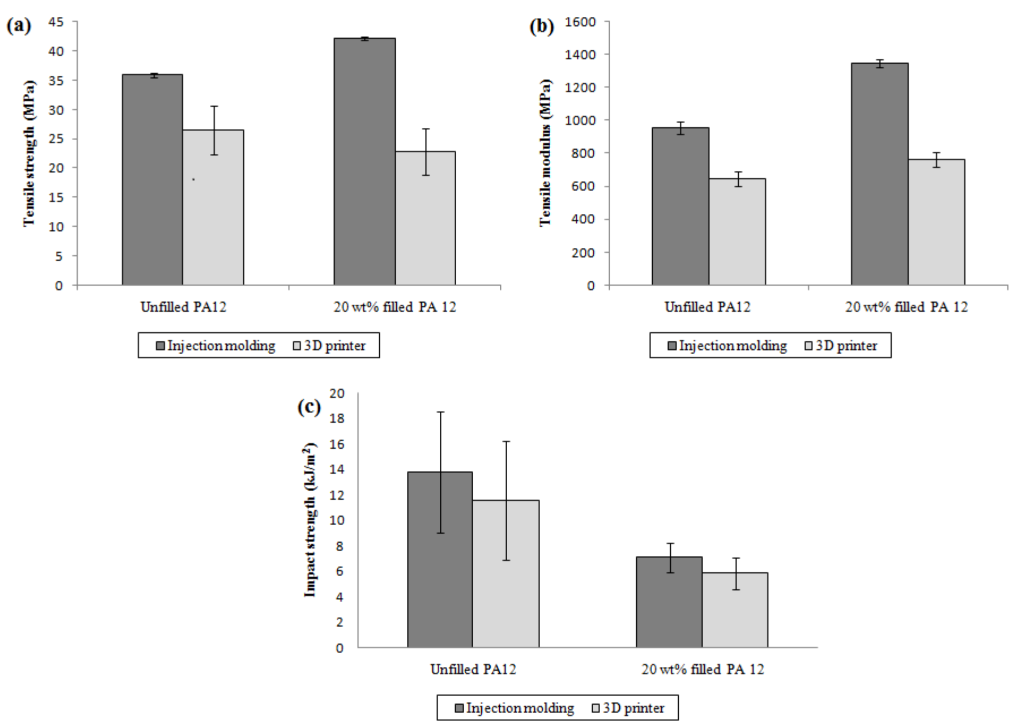

Figure 2 Mechanical properties of PA and PA/ZrO_2/HA composite prepared by injection molding and desktop 3D printer: (a) tensile strength, (b) tensile modulus, and (c) impact strength.

When comparing of two techniques used, both strength and modulus of printed PA reduce approximately 20-40 % compared with injection molded PA. In fact, the decrease in mechanical properties from 3D printing specimen can be expected. This is because the printed part was built in layers, which means it has laminate weaknesses between the layers. At a same time, the printed part was also built with lower pressure compared with injection molding, which produces a part with high porosity, hence lowering the mechanical properties.
Although the properties of printed part are not equivalent to the parts produced from injection molding, 3D printing is the special tool that capable to produce a specific design part without requiring of expensive tooling, molds or dies. Other technique of 3D printing also shows lower mechanical properties compared with injection molding [7]. However, the printed material still can be applied as long as its properties adequately sustain the high load-bearing and conform to the biomedical application. Cortical bone and cancellous bone exhibit tensile strength of 52-133 and 7 MPa, respectively.

Meanwhile, commercial implant such as PMMA exhibit tensile strength of 59 MPa [8]. In this study, the strength of PA obtained was still lower than expected for high load-bearing application. Nevertheless, the results obtained could be the first step to explore more about the potential of manufacturing biomedical implant by using this technology. For the future improvement, some parameters of 3D printer can be adjusted to increase the material properties including layer height, percentage of infill, number of shells and speed while extruding and traveling.

3.3 Morphological Properties

Figure 3 and 4 depict the fractured surface of tensile specimen prepared by injection molding and desktop 3D printer. The smooth surface of fractured specimen can be observed for unfilled PA, corresponding to ductile fracture. Polymer chains were aligned each other and highly oriented during the drawing deformation. Incorporation of fillers limits the arrangement of polymer chains, and therefore composite tend to break earlier. In comparison to the fractured surface of printed specimen, the difference of PA morphology can be observed. This difference decreases the ductility in PA, thereby lowering the mechanical properties. Figure 4(b) shows the porous of printed PA composite which can be a place for stress concentration. It was assumed the porous structure was formed due to absorption of moisture from environment through a porous and very fine hydroxyapatite filler. During the processing in 3D printer, the moisture would turn to steam and form the extrudate that contain bubbles in the thread.

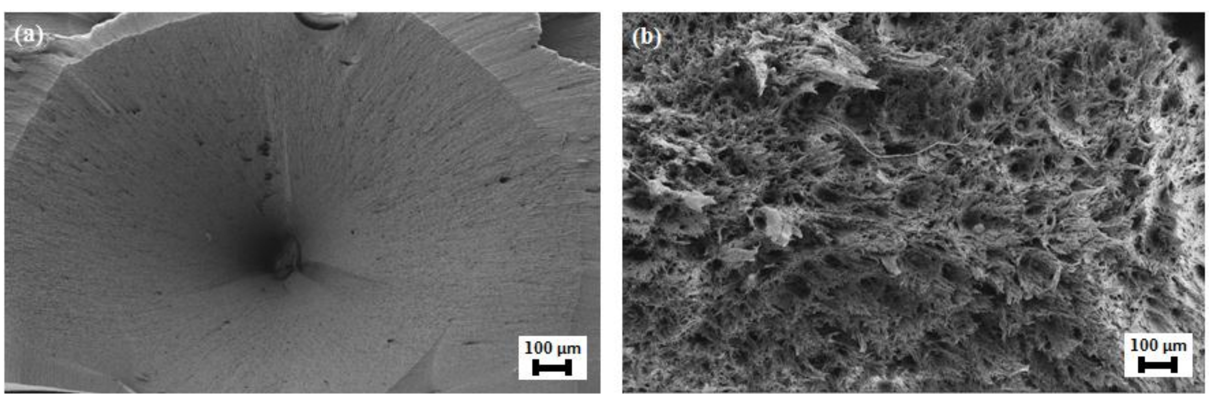

Figure 3 Fractured surface of injection molded specimens: (a) unfilled PA and (b) 20 wt% filled PA.

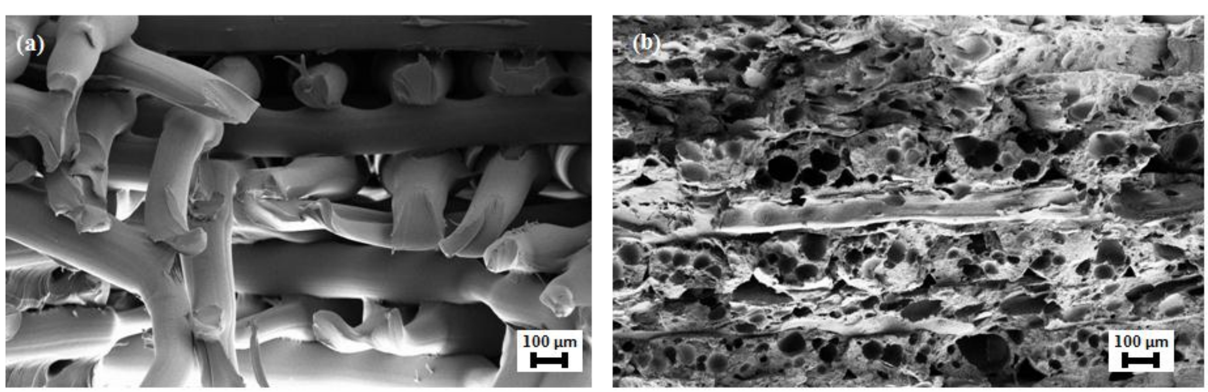

Figure 4 Fractured surface of printed specimens: (a) unfilled PA and (b) 20 wt% filled PA.

4.0 CONCLUSION

A feasibility study was performed to explore the potential of using a desktop 3D printer as a fabrication method of polyamide composite for biomedical implant. Mechanical properties of polyamide made by 3D printer was compared with a conventional manufacturing method, injection molding. Based on the findings of this study, the differences in the mechanical properties could be related with several factors including morphological change, processing pressure and presence of fillers. Considerations should also be made for changing parameters of printer used, so that functionally strong parts can be created through a desktop 3D printer.

Acknowledgement

The authors gratefully acknowledge Universiti Sains Malaysia for the financial support of RUT grant 1001/PPSG/852004. First and third authors are supported by MyBrain15 Program under the Malaysian Ministry of Education.

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