Polyhydroxybutyrate/polylactic acid blends: An alternative feedstock for 3D printed bone scaffold model

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Abstract. In this research, we developed 3D printing filaments from polyhydroxybutyrate (PHB)/poly(lactic acid) (PLA) blends to further its use in a fused filament fabrication (FFF) 3D printing technique as an alternative feedstock for manufacturing bone scaffold model. The filaments were fabricated with blending ratios of PHB/PLA at 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100 %wt. using an extrusion process. Furthermore, 10 phr of polypropylene glycol (PPG) was added as a processing aid to enhance the processability. The results of MFR showed that the suitable temperature for 3D printing of all blended filaments is 190 °C. The changes in thermal properties indicate the partial compatibility between PHB and PLA in the blends. PLA plays a vital role in improving the mechanical properties of PHB. 3D printing filament from PHB/PLA blends has been successfully developed.

1. Introduction
Bone scaffold is a three-dimensional structure that can be used to regenerate bone damage. The scaffold can be bone substitute material for cell adhesion, cell division, cell proliferation, cell growth, and changes in tissue shape in which tissue was cultured. However, when the cultured cells grow and increase until there is a sufficient quantity on the cell scaffold. Then implanted in the area to be replaced, and the cells on the scaffold grow into new tissue to replace the primary tissue. At the same time, the scaffold is degraded in the body. The important properties of the scaffolds are must be compatible with the body, no resistance of the immune system, must not stimulate the body’s immune system. Also, the scaffolds should have mechanical properties suitable for each part of the bone’s function, must be strong enough to function of implantation to the completion of the remodelling process [1]. Normally the materials that can be used for fabricating the bone scaffold must be non-toxic, biocompatible, and in some cases, biodegradable. The materials must form three-dimensional similar in structure to the replacement organ. The bone scaffold can be prepared from ceramics, bioactive glasses, metals, polymers, composites. Recently, the bone scaffold is made using solvent casting; however, it cannot create a specific shape and material restriction difficult to control the porosity. Simultaneously, the bone scaffold needs to have suitable architecture and sufficient porosity with suitable size. Three-dimensional (3D) printing with a fused filament fabrication (FFF) system is a fascinating technique for bone scaffold preparation due to its low cost and ease of producing the part with customizing [2]. With FFF 3D printing, complex structures can be easily created [3-4].
Poly(3-hydroxybutyrate), PHB, is an interesting biopolymer with good biocompatible and presents high crystallinity, which has been widely used for biomedical applications, such as bone plates, screws, orthopedic pins, bone marrow scaffolds and meniscus regeneration devices [5-7]. PHB scaffolds showed an ability to sustain cell growth to support tissue formation thereby might be considered for tissue engineering applications. The limitation of PHB is the brittleness and poor processability [8]. Polymer blending is one of proposing techniques for overcoming the limitation of PHB. Polymer blends are mixtures of at least two polymers or copolymers, which are expected to exhibit advantageous properties that each polymer does not have. The properties of the blends depend mainly on thermodynamic miscibility [9]. PLA is another interesting polymer applicable for fabricating bone scaffold according to its biocompatibility, biodegradability, and good mechanical properties. Moreover, it is widely used in FFF 3D printing allocation [10]. Gonzalez Ausejo et al. reported that PHB/PLA blend exhibited good biocompatibility with HEK293 cells, indicating real promise as biological scaffolds for tissue engineering applications. However, the blends still have difficulty in processing [11]. As a result, plasticizers are normally introduced to the blend system to enhance processability [12]. Polypropylene glycol, PPG, is mostly used due to its low cost and non-toxic property. PPG shows good solubility, high chemical stability, biocompatibility, and biodegradability [13-14]. This study aims to develop a biodegradable 3D printing filament from PHB/PLA blends for potential use for fabricating the bone scaffold model. PPG is incorporated into the blends to improve their processability. The flowability, thermal and mechanical properties of all blend compositions are investigated. Furthermore, the appropriate 3D printing condition for bone scaffold fabrication is explored.

2. Experimental Procedure

2.1 Materials
PHB (ENMAT Y3000P) was purchased from TianAn Biologic Materials Co. Ltd., China and PLA (4043D) was supplied from NatureWork, USA. PPG (DL1000P) obtained from IRPC Public Company Limited was used as the plasticizer.

2.2 Filament fabrication
In order to prepare 3D printing filaments, the materials at a composition given in table 1 was extruded using twin screw extruder (Thermo PRISM DSR-28, L/D 25:1) at 170°C and screw speed of 30-90 rpm. The extrudate was passed through water before wound up by adjustable speed wind-up machine and to control size of filaments at 1.70-1.85 mm.

| Formular       | PHB (% wt) | PLA (% wt) | PPG (phr) |
|----------------|------------|------------|-----------|
| 1. Neat PHB    | 100        | -          | -         |
| 2. PHB_PPG     | 100        | -          | 10        |
| 3. PHB90_PLA10 | 90         | 10         | 10        |
| 4. PHB70_PLA30 | 70         | 30         | 10        |
| 5. PHB50_PLA50 | 50         | 50         | 10        |
| 6. PHB30_PLA70 | 30         | 70         | 10        |
| 7. PHB10_PLA90 | 10         | 90         | 10        |
| 8. PLA_PPG     | -          | 100        | 10        |
| 9. Neat PLA    | -          | 100        | -         |

Table 1. The composition of blended filaments.
2.3 3D printing of specimen by FFF 3D printer

The flexural specimens were printed into rectangular shape by FFF 3D printer (Duplicator 6 PLUS, Wanhao, China) following ASTM D790 using the 3D printing condition showed in table 2. The dimension of the specimen was 63.5 mm x 12.7 mm x 2 mm. Five specimens were printed. The specimens were printed using the nozzle diameter of 0.4 mm, layer height of 0.2 mm, infill density 100%, print speed 25 mm/s, printing temperature 190 °C and build plate temperature 40 °C.

3. Characterization

3.1 Thermal properties

A differential scanning calorimeter (DSC, 822e, Mettler toledo, USA) was conducted to evaluate transition temperatures including glass transition temperature ($T_g$) and melting temperature ($T_m$) of filaments. The carrier gas was nitrogen. The scanning process comprised of initial heating from 30-200 °C at 5 °C min$^{-1}$, followed by cooling from 200-30 °C at 5 °C min$^{-1}$, and second heating from 30-200 °C at 5 °C min$^{-1}$.

3.2 Melt flow rate

A pseudo-melt flow rate of all filaments was carried out using a FFF 3D printer (Duplicator 6 PLUS, Wanhao, China), with the nozzle diameter of 0.4 mm in order to examine the appropriate printing temperature. The extrudate in a 30-seconds time frame at different printing temperatures of 180, 190, 200, 210, and 220 °C was weighed and presented in a unit of g/10min.

3.3 Mechanical properties

Flexural testing was performed using Universal testing machine (H10KM, Hounsfield (Tinius Olsen), USA) following ASTM D790, at a testing speed of 50 mm/min, and support span of 32 mm.

4. Results and Discussion

4.1 Thermal properties: Differential scanning calorimeter (DSC)

Fig. 1 showed the second heating scan for all filaments. Neat PHB filament showed the melting temperature ($T_m$) at 173 °C. The glass transition temperature ($T_g$) was around 5 °C [12]. Thus, it cannot be observed in our measurement temperature range. Neat PLA filament showed $T_g$, cold crystallization temperature ($T_{cc}$), and $T_m$ at 57 °C, 110 °C and 147 °C, respectively.

![DSC thermogram of neat PHB, neat PLA, PHB_PPG, PLA_PPG, and PHB_PLA blends.](image-url)
With PPG addition, $T_m$ of the filament (PHB_PPG) shifted to the lower temperature from 173 ºC to 170 ºC of PHB. Similarly, after adding PPG into the neat PLA, $T_g$, $T_{cc}$ and $T_m$ peaks tended to shift to the lower temperature, i.e. 57 to 55 ºC for $T_g$, 110 to 106 ºC for $T_{cc}$ and 147 to 145 ºC for $T_m$. This could attribute to the plasticizing effect of PPG, which enhancing the polymer chains mobility. The PPG molecules were dispersed in PHB and disturbed the crystal formation, therefore reducing the melting temperature of PHB [15]. PHB/PLA blends exhibited two melting temperatures ($T_m$) because PHB and PLA are not miscible. As shown in Fig.1, $T_m$ of the blends with high PHB contents (PHB70_PLA30 and PHB90_PLA10) tended to shift to the lower temperature, close to $T_m$ of the neat PLA. In contrast, $T_m$ of the blends with high PLA contents tended to shift to a higher temperature. These results may be due to the partial compatibility between PHB and PLA in the blends. It should be noted that for PHB90_PLA10, only a small endothermic melting peak at 170 ºC was observed indicating a higher degree of compatibility for this blend composition. Furthermore, the shifts of $T_{cc}$ to lower temperatures were observed with increasing PHB contents, indicating the more favor of PLA crystallization. A similar behavior was also found for PLA_PPG, which may be attributed to low molecular weight products, increasing the polymer chains mobility and favors PLA crystallization [16].

4.2 Melt flow rate (MFR)

In general, the mechanical properties of the sample depended on the printability of the specimen, which was directly influenced by the flowability of materials at a specific temperature. Therefore, the MFR of materials was evaluated using a 3D printer to determine the printing temperature suitable for printing. The MFR information can be used as a guideline for setting up the printing parameters [17-18]. Fig. 2 showed the MFR of all neat polymer and blends at 5 different temperatures from 180 – 220 ºC. It can be seen that PHB10_PLA90 and PHB70_PLA30 exhibited the most stable flow, particularly in the temperature range of 190-210 ºC. This could be implied that the suitable printing temperature to give a stable material flow for PHB90_PLA10 and PHB70_PLA30 were in a range of 190-210 ºC. Consequently, all blends showed almost similar flowability at 190 ºC. Thus, the nozzle temperature will be set at 190 ºC during the 3D printing process.

![Fig. 2 MFI of neat PHB, neat PLA, PHB_PPG, PPLA_PPG, and PHB_PLA blends.](image)

4.3 Mechanical properties: Flexural strength

PHB and PLA showed the flexural strength of 35.6 ± 1.86 MPa and 99.8 ± 10.11 MPa, respectively. PHB_PPG could not be printed because of unstable flow and high warpage. Moreover, poor compatibility between PHB and PPG might affect poor printability. After interblending between PHB and PLA with various ratios, the PHB10_PLA90 showed lower flexural strength and modulus than neat
PHB and neat PLA due to poor compatibility between PHB and PPG. PHB70_PLA30 showed better flexural strength and modulus due to higher compatibility between PLA and PPG compared to PHB and PPG. Although PHB50_PLA50 contains a higher content of PLA, flexural strength and modulus were compared with PHB70_PLA30 because at the ratio the occurrence of phase separation between PHB and PLA might be occurred. For the PLA-rich blend, increment of flexural strength and modulus was depended on the percentage of PLA. The PLA-rich blend including, PHB10_PLA90 and PHB30_PLA70, showed lower flexural strength and modulus compared to neat PLA, as showed in Fig. 3A and 3B. For the PHB-rich blends, the recommended PLA content is 30wt%. For PLA-rich blend, either 10 or 30wt% of PHB could be blended with PLA, which the mechanical properties are still acceptable.

![Fig. 3 Flexural strength (A) and Flexural modulus (B) of neat PHB, neat PLA, and PHB_PLA blends.](image)

5. Conclusions

In this work, 3D printing filament from PHB_PLA blends has been successfully developed. The thermal properties indicated the partial compatibility between PHB and PLA in the blends. The MFR of the neat PLA, PHB10_PLA90, and PHB70_PLA30 remained almost constant. The stable flowability was observed at the nozzle temperature at 190 °C, thus, it was selected as a suitable printing temperature for all blends and the neat polymers. The PHB-rich blends exhibited lower flexural strength and modulus compared to the PLA-rich blends. PLA can thus be used to improve the mechanical properties of PHB. PHB10_PLA90 and PHB30_PLA70 were the appropriate blending compositions to fabricate 3D printing filament with improved mechanical performance. Also, PHB10_PLA90 and PHB30_PLA70 blends exhibit suitable properties for further used to fabricate 3D printed bone scaffold.

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