# Polylactic acid/poly-3-hydroxybutyrate applications in Extrusion based Additive Manufacturing

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ABSTRACT: Polyhydroxybutyrate (PHB) is a polyhydroxyalkanoate (PHA), a polymer belonging to the polyesters class that are of interest as bio-derived and biodegradable plastics. PLA is a biodegradable material widely used in 3D printing. In this research, PHB/PLA filaments were produced to be used in extrusion based additive manufacturing. It was found, when adding more PHB into the PLA/PHB blend, samples can be 3D printed under lower temperature, thus saving energy. PHB has a bad adhesion on the printing bed due to warpage and shrinkage. Blending with PLA can solve this adhesion problem. Besides adhesion, modulus and tress at break increased when adding PLA. Elongation at break reached maximum with a PHB content of 40wt% as pure filament, while it showed highest value with 20wt% PHB for printed tensile bars. The impact strength increased slightly when adding PLA and reached maximum with 20wt% PHB. VST of PLA/PHB blend was always above 150°C due to the good crystallization effect of PHB.

## 1 INTRODUCTION

3D printing or additive manufacturing (AM) is a manufacturing process that enables the production of physical objects directly from digital part models by additive processes, whereby successive layers of materials are deposited to fabricate the final parts. Extrusion-based AM such as fused filament fabrication (FFF), also known as fused deposition modeling (FDM), is a widely used, low-cost technique［Swetham, et al. 2017］. AM with polymers has been exploited in a number of innovative ways to produce materials and functional devises in many fields. A major challenge of extrusion-based AM is the lack of commercially available materials［Spoerk, et al. 2018］compared to those in well-established processes like injection molding or extrusion.

Poly(3-hydroxybutyrate) (PHB) is a biodegradable thermoplastic with biocompatibility and ecological safety［Sharma, et al. 2016］and can be extruded, molded and spun using conventional plastic processing equipment［Arrieta, M. P., et al. 2014］. Biosourced PHB are used in 3D printing to broaden the material pool for FFF. PLA, also a biodegradable polymer is used to improve the printing and mechanical properties of PHB. Many people investigated the PLA/PHB blend for food package or other applications［Arrieta, Marina P., et al. 2014］, but PHB and PHB/PLA blend used in 3D printing have not yet been done. Within this research, filaments of PHB/PLA blends were produced and processed via extrusion based AM. Afterwards, mechanical and thermal properties were characterized.

## 2 EXPERIMENTAL

### 2.1 *Sample preparation*

Polyactic acid (PLA 3D850) pellets, a grade developed for manufacturing 3D printer monofilaments, was purchased from Natureworks. Polyhydroxybutyrate (PHB P304) pellets were obtained from Biomer. Materials were dried over night at 45°C before processing.

PHB/PLA blends with different compositions (80/20, 60/40, 40/60, 30/70, 20/80 by mass ratio) were produced into granules via twin screw extruder (Coperion ZSK18ML) with a screw diameter of 18 mm and L/D 40. A screw speed of 120 rpm and a temperature profile from 155°C to 190°C was used. The extrudates were water cooled and cut into granules for the next processing step in the single screw extruder (Brabender PL2000 - screw diameter 19 mm and L/D 25) to fabricate consecutive filament with diameter of 1.75mm. The temperature profile was 160, 170, 180 and 190°C from feeding zone to die. The screw speed was set 30 rpm and hauling speed 8 m·min$^{-1}$, allowing a uniform filament diameter. Pure PHB and PLA filaments were also produced under same condition with processing temperatures up to 185°C and 210°C, respectively, according to the processing temperatures mentioned in the corresponding datasheets. Blend was denoted as PHB/PLA x/y (e.g. PHB/PLA 80/20). All the produced filaments were dried overnight at 45°C to remove the moisture.

The produced filaments were printed on a Felix 3.0 printer at a flow speed of 50 mm·s$^{-1}$. PHB and its blends were printed at 180°C, PLA was printed at 210°C, and bed temperature was set as 55°C. The nozzle diameter was 0.35 mm. The layer thickness was set at 0.15 mm, infill rate of 100% and a crossed 45° raster printing angle were used. A dog-bone sample (type 1BA) was applied to tensile test according to ISO527. A rectangular sample (80×10×4 mm$^3$) based on ISO 179 was applied to test the Charpy impact strength of printed part.

## 2.2 *Melt flow index*

The rheology of the blends are characterized via melt flow index (MFI) test. Samples are tested under certain temperature (180 to 210°C) with a load of 2,16 kg referring to ISO 1133.

## 2.3 *Mechanical analysis*

Tensile property of filaments and printed bars were measured on an Instron 5565 machine with a force of 5 kN in combination with the Blue Hill software. The measurements are performed according ISO 527. The extensometer 2620-603 Instron with Gauge length 25 mm is used to calculate accurate results at the beginning of the stress-strain curve. A 1 mm·min$^{-1}$ tensile rate is applied until 0.3% strain for determining the Young's modulus. Afterwards 5 mm·min$^{-1}$ is executed until the material breaks. Impact tests were conducted on a Tinius Olsen Impact model 503. Dimension of specimen was as described in the Charpy ISO 179 standard. A V-notch was applied with a depth of 2 mm. The weight of pendulum was 0,462 kg, which supplies a nominal impact energy of 2,82 J and a released velocity of 3,46 m·s$^{-1}$. All tests were carried after 2 days conditioning in standard atmosphere (23°C and 50% humidity). At least five samples were tested to get an average value.

## 2.4 *Thermal analysis*

To know the crystallization behavior of different samples, DSC measurement was taken on the DSC machine (NETZSCH 204 F1). Samples were heated from room temperature to 200°C and kept at such temperature for 5 min to erase the heat history, then cooled to 20°C at cooling rate of 10°C min$^{-1}$ and heated up to 200°C again at heating rate of 10°C min$^{-1}$. Crystallization peak ($T_c$) and enthalpy ($\Delta H_c$) were recorded from first cooling curve. Cold crystallization peak ($T_{cc}$) and enthalpy ($\Delta H_{cc}$), melt peak ($T_m$) and fusion enthalpy ($\Delta H_m$) can be recorded from second heating curve. To know the effect of printing history on samples, printed bars were heat from 10°C to 200°C at 10°C min$^{-1}$, heating curves were recorded.

The Vicat softening temperature (VST) of the samples were investigated using a thermal deformation, Vicat softening temperature tester (CEAST 6510). Printed samples with same dimension of impact bars were used to determine the Vicat softening temperature. The test was performed in accordance with ISO306:1994 in methyl silicone oil bath at a heating rate of 120°C·h$^{-1}$ under a specific load of 10N.

# 3 RESULTS AND DISCUSSION

## 3.1 *Melt flow index*

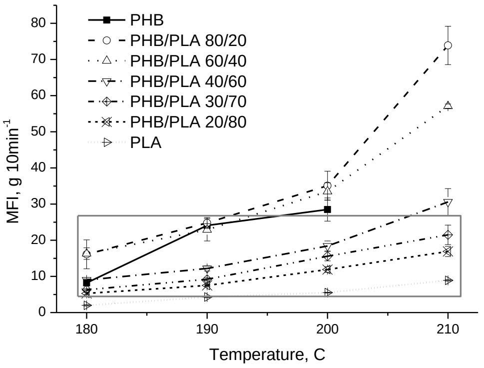

Figure 1. Melt flow index of samples at different temperature.

Rheological data is an important parameter for 3D printing applications to achieve a good and stable flow [Ramanath, et al. 2008, Wang, S., et al. 2017]. MFI data for samples at different temperatures were measured; results were shown in Figure 1. MFI value increases with testing temperature. MFI increases from 2.0±0.2 to 8.6±0.5 g·10min$^{-1}$ for PLA filament at temperature from 180 to 210°C. The MFI value of PHB and PHB/PLA blends are much bigger than that of PLA, and it increases a lot with testing temperature. It is noticed that PHB is more sensitive to temperature than PLA. Based on 3D printing pretests, samples can be printed in the area shown in black rectangle in figure 1. PHB and PHB/PLA can be printed under lower temperature compare to PLA, thus saving energy. Based on the previous research[Wang, S., et al. 2017], it is recommended to print samples with a MFI value close to/above 10 g·10min$^{-1}$. Based on this investigation, pure PHB and blends were printed at 190°C, pure PLA was printed at 210°C.

During the tests it was found PHB has a bad adhesion on the printing bed due to warpage and shrinkage. The adhesion improved with blends containing PLA or when printing on blue tape. Blends which contain less than 60*wt*% PHB were printed on standard printing bed.

## 3.2 *Mechanical property*

Tensile and impact data of samples were shown in figure 2 and table 1. As expected, the properties of printed bars are not as good as that of the filaments due to the existence of voids in printed parts[Wang, L., et al. 2017]. Modulus and stress of samples increase with more PLA in the blend because of the high tensile modulus and strength of PLA[Jalali, et al. 2016]. Similar results can be seen in other studies[Bartczak, et al. 2013]. Pure PHB and PLA showed low elongation, while toughness of blends increased slightly compared to pure material. Elongation at break reached maximum with a PHB content of 40wt% for filament, and it showed highest value with 20wt% PHB for printed tensile bars. The slight increment of elongation is due to the poor miscibility between PLA and PHB[Lin, et al. 2016]. To improve the tensile property even more, the morphological structure of the blend should be modified in future studies. The impact strength increased slightly when adding PLA and reached maximum with 20wt% PHB. Bartczak [Bartczak, et al. 2013] and Lai[Lai, et al. 2017] investigated the toughness of PLA/atactic PHB (a-PHB) blend, finding a significant increase in the ductility of blend because of the plasticization effect of a-PHB.

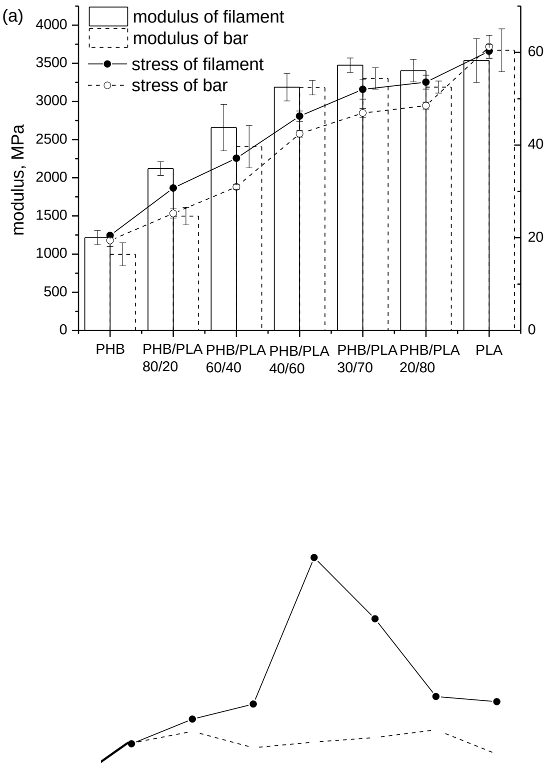

Figure 2. Mechanical properties (a) modulus and stress at maximum load, (b) Charpy impact strength and strain at break for filament and printed bars.

Table 1. Mechanical data of PHB/PLA blends.

| Sample | Modulus, MPa | Stress at maximum load, MPa | Strain at break, % | Charpy impact strength, kJ·m$^{-2}$ |
|---|---|---|---|---|
| | | filament | | |
| PHB | 1215±94 | 20.5±0.4 | 5.3±0.2 | - |
| PHB/PLA 80/20 | 2121±91 | 30.7±0.3 | 10.5±0.5 | - |
| PHB/PLA 60/40 | 2658±305 | 37.2±0.4 | 13.6±4.7 | - |
| PHB/PLA 40/60 | 3187±180 | 46.2±1.1 | 44.1±12.0 | - |
| PHB/PLA 30/70 | 3475±95 | 52.0±2.1 | 31.3±12.6 | - |
| PHB/PLA 20/80 | 3404±147 | 53.6±1.5 | 15.2±10.2 | - |
| PLA | 3537±288 | 60.3±1.5 | 14.1±7.2 | - |
| | | Printed bar | | |
| PHB | 997±151 | 19.4±1.3 | 5.5±0.3 | 3.5±0.6 |
| PHB/PLA 80/20 | 1498±115 | 25.3±1.0 | 7.9±1.5 | 3.1±0.4 |
| PHB/PLA 60/40 | 2408±277 | 31.0±0.5 | 4.5±0.5 | 3.1±0.4 |
| PHB/PLA 40/60 | 3182±95 | 42.4±0.7 | 5.7±1.4 | 3.6±0.9 |
| PHB/PLA 30/70 | 3303±140 | 46.9±1.0 | 6.6±1.1 | 4.3±0.2 |
| PHB/PLA 20/80 | 3189±79 | 48.5±0.7 | 8.2±2.2 | 5.0±0.5 |
| PLA | 3671±280 | 61.2±2.5 | 3.2±0.5 | 4.2±0.5 |

In general, PHB/PLA 20/80 showed best mechanical properties among all these samples. Mass ratio of 20/80 can be used to acquire samples with good mechanical properties.

### 3.3 *Thermal property*

DSC curve of filaments and printed bars were shown in figure 3. In figure 3(a), there is sharp crystalline peak ($T_c$) in the cooling curve for PHB (115.0°C), which means PHB has good melt crystallization ability. $T_c$ shift to lower temperature after PLA was added (108.1°C for PHB/PLA 20/80), which means melt crystallization ability of blend weaken. Pure PLA has no crystalline peak, which means it crystallizes very slow during the cooling process［Jalali, et al. 2016］. In figure 3(b), PLA shows a big cold crystallization peak but as for PHB no cold crystal peak has been noticed in the second heating curve, confirming PHB's good crystallization ability. The PHB/PLA blends show similar crystallization behavior to pure PHB, confirming the nucleating agent of PHB on PLA, which significantly improves the melt crystallization ability of PLA3D［Arrieta, M. P., et al. 2014］. The melting point of PHB is smaller than PLA, which results in a bigger MFI for the blend, as discussed in section 3.1.

DSC results of printed bars are illustrated in figure 3(c). Pure PHB and PHB/PLA blends contain more than 60*wt*% PHB have no cold crystal peak and the glass transition platform looks flat, indicating high crystallinity of printed samples which may be unfavorable to the printing quality. As pretest of 3D printing showed, blends contain more PHB will warp and cannot adhere to platform well. So to obtain a well printed part, less than 60*wt*% of PHB should be used. With higher percentage addition of PLA, the glass transition temperature ($T_g$) and cold crystallization temperature ($T_{cc}$) shift to the right and the cold crystallization peak becomes bigger, which means a decreased crystallization ability and lower crystallinity of the blends. This means that PLA with low crystallinity is not suitable for heat resistance applications.

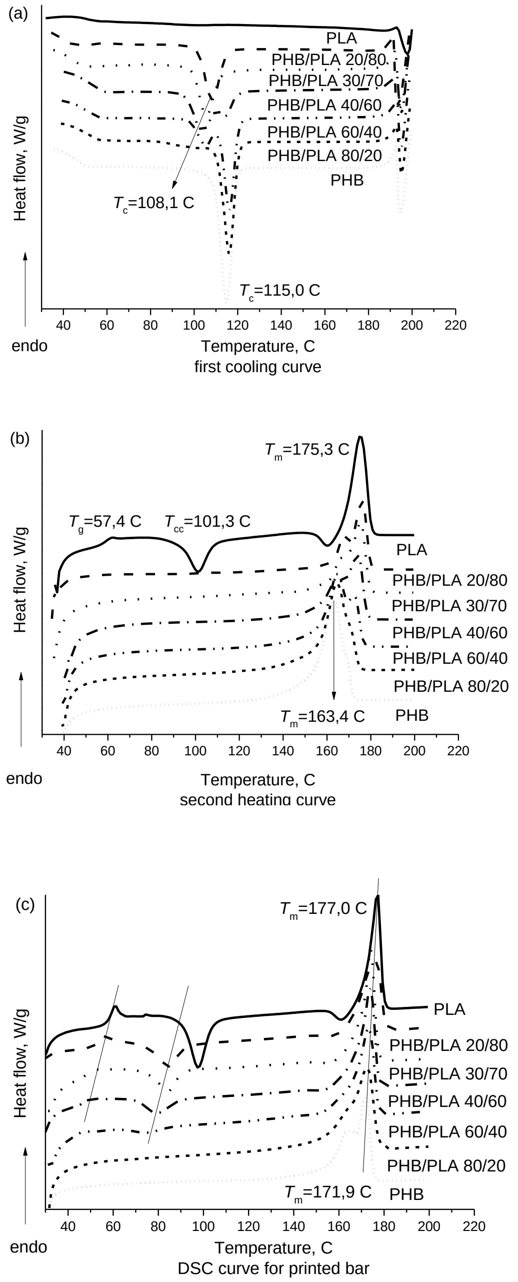

Figure 3. DSC curve (a) first cooling, (b) second heating curve of filaments, (c) DSC curve for printed bars.

Vicat softening temperature (VST) of PHB/PLA was measured in following part to know the heat resistance of the samples. Pure PHB and samples with PHB inside always showed a VST above 140°C due to the good crystallization effect of PHB. Pure PLA has a rather low VST (61.6°C) due to its low glass transition temperature and the slow crystallization rate unless it is fully crystallized［Jalali, et al. 2016, Tsuji, et al. 1995］. By adding PHB, PLA can obtain a higher crystallinity, as it can sufficiently crystalize during the cooling phase of the printing process, which can lead to better heat resistance and strength.

According to the DSC and VST results, PHB has a fast crystallization during printing. Pure PLA has a slow crystallization resulting in poor heat resistance, while PHB/PLA blends showed good thermal performance.

Table 2. Vicat softening temperature of PHB/PLA blends.

| sample | PHB/PLA | | | | | | |
|---|---|---|---|---|---|---|---|
| Mass ratio | PHB | 80/20 | 60/40 | 40/60 | 30/70 | 20/80 | PLA |
| VST, °C | 146.6 | 143.8 | 153.3 | 152.9 | 153.0 | 153.4 | 61.6 |

## 4 CONCLUSION

Bio-based PHB/PLA filaments used in extrusion based additive manufacturing were developed and characterized. It was found, when adding more PHB into the PLA/PHB blend, melt flow index drops and samples can be 3D printed under lower temperature, thus saving energy. PHB has a bad adhesion on the printing bed due to warpage and shrinkage. PLA was added to improve the adhesion. It was found that PHB content should not be more than 60*wt*% to get samples with good printing quality. Modulus and stress at break increased a lot after adding PLA thanks to PLA's high stiffness. Elongation at break reached maximum with a PHB content of 40wt% as pure filament, while it showed highest value with 20wt% PHB for printed tensile bars. The impact strength increased as well when adding PLA and reached maximum with 20wt% PHB, which is comparable for tensile strain. VST of PLA/PHB blend was always above 150°C due to the good crystallization effect of PHB.

In summary, more PHB will lead to higher crystallinity, better heat resistance, and consume less energy by printing at lower temperature. However, pure PHB is not a good candidate for low cost extrusion based AM. To obtain samples with good printing quality and good mechanical properties, PLA should be added. PHB/PLA 20/80 blend showed best general performance, which can be considered as a potential blend for 3D printing in future research.

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