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Characterization of 3D Printed Poly(3-Hydroxybutyric-Co-3-Hydroxyvalerate) by Fused Granular Fabrication through Thermal and Mechanical Analyses

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Abstract

Poly[R-3-hydroxybutyrate-co-(R-3-hydroxyvalerate)] (PHBVs) copolymers are promising biopolymers, which could substitute petroleum-based plastics for various applications. PHB and PHBV pellets were processed on a customized 3D printer via Fused Granular Manufacturing (FGM) approach modified with a Mahor screw extruder. To anticipate the behaviour of PHBVs when transformed using conventional thermo-mechanical shaping processes, thermal and mechanical analyses were carried out in order to better understand the effect of annealing temperature on their crystallization behaviour and mechanical properties of PHB polymer and PHBV copolymer. The objectives of the present work were to propose an experimental strategy to study the melting and crystallization events, crystalline structure changes, and mechanical performances of both PHB homopolymer and PHBV copolymer according to identical thermal annealing treatments. A monitoring of 3D printed PHB and PHBV structures was achieved by coupling Differential Scanning Calorimetry (DSC) and tensile tests.

Keywords

Additive Manufacturing, 3D Printing, Biodegradable Plastic, Fused Granular Manufacturing, Poly[R-3-Hydroxybutyrate-Co-(R-3-Hydroxyvalerate)]

1. Introduction

Fused Deposition Modelling (FDM) and Fused Filament Manufacturing (FFM)

are commonly referred to as typical 3D printing technique. The material is loaded onto the machine in the form of thermoplastic filaments that are extruded through a nozzle and deposited layer-by-layer on a printing platform [1]. Despite the ever-growing popularity of 3D printing due to relatively inexpensive material and equipment costs, the requirement of an intermediate polymer filament production step causes significant inefficiencies in the production process of 3D printed objects. Therefore, a more cost-effective approach involves the use of pellets directly as raw material for 3D printing, rather than for filament production. This alternative solution is the pellet-extrusion technology for additive manufacturing known as Fused Pellet Manufacturing (FPM) or Fused Granular Manufacturing (FGM). The main benefits of FGM compared to FFM are based on avoiding the filament manufacturing and therefore the possibility of altering polymer properties during the fabrication due to thermal effect, but also avoiding the strict dimensional controls of the filament diameter request to minimize warping, creep or blocking of material in the 3D printer's feed mechanism [2]. Moreover, the storage of pellets is easier than for filaments, which are wound into spools, causing a waste of material. In particular, the initial section of the filament, which is wound with a narrow winding radius, is subjected to residual stress that can embrittle less ductile materials. Two other limitations of filament-based 3D printing are the limited choice of thermoplastic polymers available on the market, as well as their price, which is at least five times higher than polymer pellets [3]. Moreover, by eliminating the filament creation process, it is much easier, after a simple pelletizing step, to directly recycle plastic waste in an additive manufacturing process from an economic perspective [4]. In previous scientific research, two forms of FGM have been hypothesized and examined: a plunger-based and a screw-based one. The former uses a device similar to a syringe; for instance, Volpato *et al.* extruded molten Polypropylene (PP) grains from a heated reservoir employing a cylinder-piston system [5]. However, most researchers employed the screw-based approach for constant feeding of the 3D printer. Reddy *et al.* investigated the key impact of FGM process parameters on different final properties of 3D printed objects, such as their mechanical strength and the quality of the surface [6]. An experimental screw-type extrusion system was realized by Valkenaers *et al.* and they applied it with a 0.2 mm nozzle for printing Polycaprolactone (PCL) [7]. Tseng *et al.* designed and constructed a similar system that could reach very high temperatures for processing, especially for technopolymers, e.g. Polyether Ether Ketone (PEEK) [8], whereas Whyman *et al.* presented a machine that was also equipped with an automatic feeder [9]. Woern *et al.* looked at the possibility of using recycled particles for four different thermoplastics [10]. Reich *et al.* did a similar study on Polycarbonate (PC) waste [11]. Liu *et al.* designed a two-stage extrusion technique to boost machine capacity and expand the use of FGM technology for the fabrication of large components. In the first step, a typical polymer extrusion plasticizing unit is employed to feed the following dosing and printing stage [12]. Byard *et al.* used Fab Labs as

a 3D printing waste recycling platform to prove the environmental and financial viability of employing FGM for large-scale products [13]. Similarly, Shaik *et al.* demonstrated the economic advantages of using pellets as raw material for the polymer additive manufacturing process [3], whereas Alexandre *et al.* demonstrated that FGM has comparable mechanical performance to FFM samples [4]. It is noteworthy that FGM process, as well as FDM, could be affected by some defects such as void formation [14], especially leading to a decrease in mechanical performance. In their study, Ferretti *et al.* optimized 3D printing parameters for minimization of material defects [15].

The main challenges associated with 3D printing PHBV are its poor thermal stability and warpage during 3D printing. In earlier stages of additive manufacturing such as Fused Filament Manufacturing (FFM) technique, warping has been attributed to poor surface adhesion and residual stresses resulting in the failure of 3D print products after undergoing rapid heating and cooling cycles.

Thermal annealing treatment is a key process for adjusting the structures of semicrystalline polymers, including the relaxation of oriented chains and the rearrangement of chain segments [16]. For instance, injection-molded parts always need annealing to regulate their microstructure and improve their impact toughness [17] [18]. Annealing treatment is also one of the key steps in which the structures of the synthetic fibers reach a new thermodynamic equilibrium, and results in improved mechanical properties and dimensional stability [19]. PHBV is one of the most important members of the PHA family, and although some works have studied the transformation process during the heating process, the transformation process during annealing is still ambiguous. To gain further insights into the phase change of 3D printed PHB and PHBV structures from thermal annealing, the structural and property differences between annealed and unannealed PHBV were comparatively investigated. Finally, the clarification of crystalline transformation may be an important point for clarifying the major features of 3D printed PHBV and PHB specimens.

Here, a customized version of a low-cost 3D printer was employed to investigate the processability of PHBV through a screw-based extrusion approach. Thermal and mechanical characterizations were conducted to assess the printing parameters of the material. This research work aims to combine the advantages of using an eco-friendly material such as the PBHV, along with a manufacturing process that can be sustainable in terms of time, energy and budget control.

2. Materials

The two most popular 3-D printing materials PHB and PHBV pellets with diameter of 1.75 mm were used in the 3D printer.

2.1. 3D Printing

A 3D printer equipped with a Mahor V4 screw-based pellet extruder for FGM technology was used in this study (schematic diagram in **Figure 1**). Furthermore,

a 500 W power supply was installed to boost the machine's heating capability. Eventually, the customized 3D printer can reach a nozzle temperature of 140˚C - 160˚C and a platform temperature of 40˚C, so that the range of polymers that can be processed in pellet form can be expanded.

As shown in **Figure 2**, the extruder's hopper is a self-replicated element, like those used in other customized 3D printers. The nozzle has a diameter of 0.8 mm. The cartesian structure and axis resolution of the machine remain unaltered. Build platform area 320 mm × 320 mm with heating coils on PI film for build plate temperature control. The motion system is CoreXY design with stepper motors, mounted with TMC2209 stepper motor driver with 256 u steps. 3D models were sliced with software Ultimaker Cura 5.2.2. And the printer was controlled with Marlin Firmware [20].

2.2. DSC Analysis

The thermal properties of both PHB and PHBV before and after annealing were studied using Differential Scanning Calorimeter DSC 8000 (Perkin Elmer, USA). All the tests were carried out on samples (1 - 5 mg) sealed in aluminum pans, and with a dry N_2 flow of 20 mL/min. A heating ramp from 25˚C to 200˚C at 20˚C/min was used to test both PHB and PHBV samples.

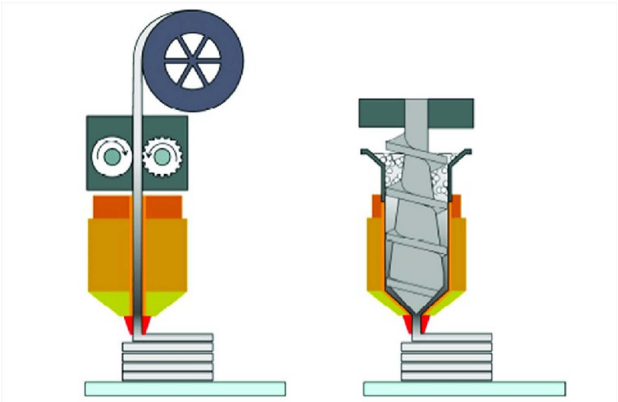

Figure 1. Schematic diagram of (a) Fused Filament Manufacturing and (b) Fused Granular Manufacturing.

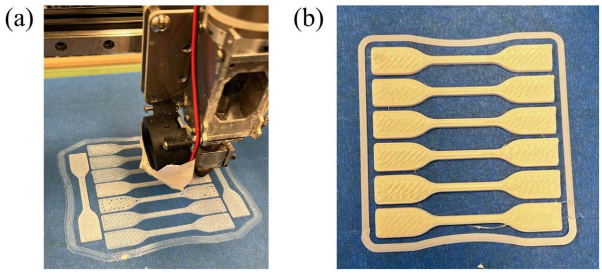

Figure 2. (a) Photo of the customized FGM 3D printer with Mahor extruder and (b) 3D printed dumbbell specimens for tensile test.

2.3. Tensile Test

To analyze the mechanical behavior of the PHB and PHBV processed by FGF, tensile tests were performed with an Instron 4411 Tensile Testing Machine (Instron, Norwood, MA, USA) on 3D printed dumbbell specimens. The tensile tests were conducted according to ISO37 standard, and specifically at a crosshead speed of 200 mm/sec. until deformation of until fracture of the sample.

3. Results and Discussion

3.1. Effect of the Thermal Annealing on the Melting-Crystallization Behavior

Figure 3 shows the melting data from the heat flow curves before and after annealing treatment, respectively. The annealing temperature and time were 130˚C and 45 min. The findings clearly show the melting enthalpy in terms of peak area was higher after annealing as compared with unannealed sample. As illustrated in **Figure 3**, three endothermic peaks were observed after annealing (labeled as T_a, T_{m1} and T_{m2} in the order of temperature from low to high). T_{m1} and T_{m2} were obviously to be identified in heat flow curve. In DSC analysis, total heat flow can be separated into the heat capacity-related (reversing) and kinetic (non-reversing) components Therefore, endothermic signals (melting) can be detected in both reversing and non-reversing heat flow scans, whereas the crystallization exotherms only contribute to the kinetic components. This exotherm presented between T_a and T_{m1} further suggested the recrystallization of crystals due to superheating ascribed to poor heat conductivity of polymer itself. From the non-reversing curve, it was found the T_{m1} shifts to slightly higher temperatures and finally merges into the highest endotherm (T_{m2}) after thermal annealing at 130˚C. T_{m1} is attributed to the melting of original crystals formed before the DSC scan, and T_{m2} is associated with the melting of the recrystallized components during heating scan. All the facts mentioned above confirmed the origin of the multiple melting behavior of PHB was probably attributed to the mechanism of melting, recrystallization and remelting during DSC reheating scan [21] [22].

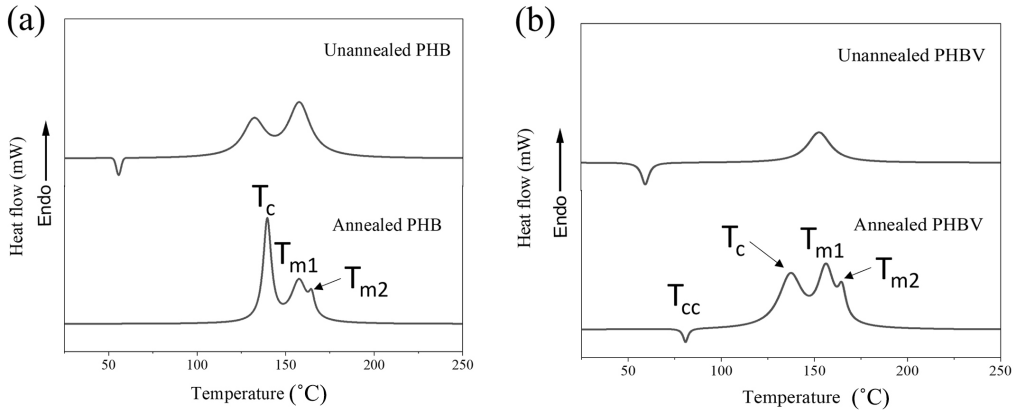

Figure 3. DSC thermograms of unannealed and annealed (a) PHB and (b) PHBV specimens.

3.2. Effect of Thermal Annealing on the Crystallinity

When measuring the crystallinity of a polymer, DSC allows for identifying the formation of crystalline structure at the initial stage of melting process. The re-crystallization is evaluated by the degree of undercooling,

$$\Delta T = T_m^0 - T_c,$$

where the T_m^0 is the ideal equilibrium melting temperature of PHB (here, T_m^0 is =157˚C determined according to the method of Hoffman and Weeks) and T_c is the recrystallization temperature (T_c = $T_{re\text{-}cry}$). The ΔT is interpreted as the driving force of recrystallization. Hence, the melt-recrystallization peak is observed after annealing treatment.

Thermal pretreatment allowed eliminating all residual nuclei in the melt, with no preferential nucleation sites, making it more difficult to reach a newly ordered structure. As a result, the nucleation and the crystallization process start at lower temperatures. It is interesting to discuss the shape of the melt crystallization peak. For PHBV, a crystallization peak was observed at 137˚C, indicating that a unique family of crystal planes formed from the melt due to self-nucleation. Melting conditions were thus adequate. After annealing at 130˚C, the crystallization peak width was broadened and became double-humped shaped, which suggested the coexistence of different crystal types. Such a split of the crystallization peak might result from the superposition of newly created crystals and crystals formed from the remaining unmelted crystals. The formation of the melt crystallization peak after thermal annealing could thus be explained by the fact that a more homogeneous crystal phase was produced from the melt phase.

3.3. Effect of the Annealing Temperature on the Re-Melting Behavior

Upon thermal annealing treatment, double melting peaks were observed and a cold crystallization temperature (T_{cc}) during the heating step (at T_{cc} = 80.8˚C) expressed in a small exothermic peak. The cold crystallization events have already been observed for PHBV before annealing [23] [24]. This supported the hypothesis of the coexistence of different crystal forms with varying thermal stability and melting temperatures. Based on all these observations, the double melting peaks observed on the heating scans after thermal annealing treatment for PHBV could be the manifestation of segregation (separation between different crystal forms) during melting-recrystallization processes. The double melting peaks observed on thermograms should be related to the existence of two different crystal phases with different melting temperatures. The first and second melting peaks (T_{m1} = 156˚C and T_{m2} = 164˚C) can reasonably be attributed to the melting of unstable crystals and recrystallization to highly stable crystals with a higher melting temperature and the melting of crystals formed through the melting-recrystallization process, respectively. For PHBV, small exothermic peak observed from annealed sample occurred at 80.8˚C compared with unannealed sam-

ple at 59.5˚C, confirming more energy is required for reorganization of crystalline structures.

The tensile test results can also be associated with the DSC outcomes. It is well known that in crystalline regions, the polymer chains have a compact structure that endures the stress and material resistance. For PHBV, HV domain is indeed expected to soften the copolymer due to higher steric hindrance of PHV units inducing a decrease of overall crystallinity, and lower stiffness. It clearly appeared that thermal annealing treatment had a significant impact on all the tensile mechanical properties of PHBV.

Thermal annealing of PHBV induced a progressive increase of the strain hardening. The difference in elongation under ultimate strength could be explained by the formation of large PHB-rich crystals from the melt-crystallization region, while PHV domains were progressively isolated and remained in amorphous phase. It should be pointed out that other degradation phenomena might be involved when processing PHBV. In particular, DSC experiments were conducted under nitrogen atmosphere, which might explain why a shift to lower critical processing temperatures was observed for hot-pressing (conducted under ambient atmosphere with possible oxidation effects) compared to critical temperatures deduced from DSC thermograms.

Regarding ultimate properties, as observed for PHBV in **Figure 4**, passing a critical temperature a large improvement of performances was observed (strain at break and stress at break passing respectively from 9.6 mm to 17.4 mm and 8.4 kgf to 9.0 kgf). The change in mechanical performance was even more pronounced than the one observed for unannealed PHBV. In the case of thermal annealed PHBV, the critical temperature inferred from mechanical testing matched well with DSC analyses. Finally, these characterizations proved the demand to extend the characterization of the polymers until practical mechanical testing of final formed materials to define a realistic processing window of 3D printed products in relation to functional properties.

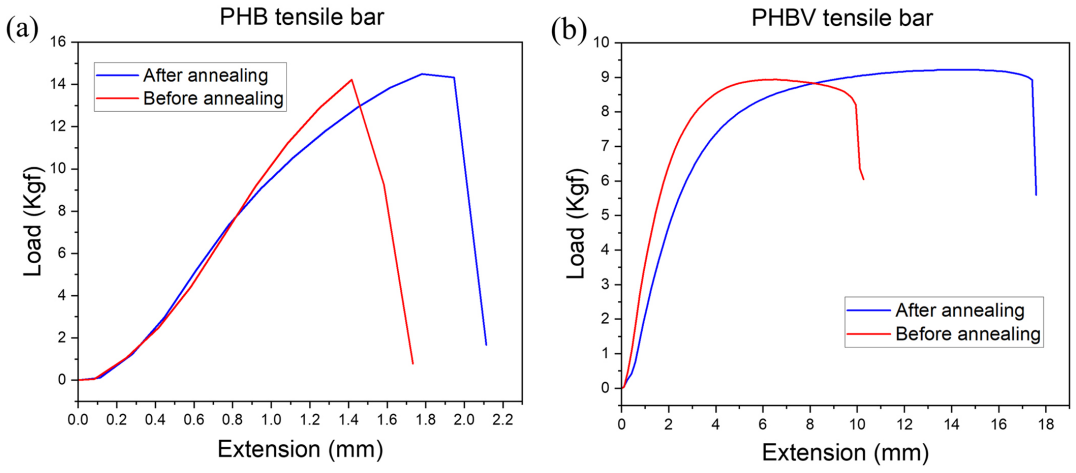

Figure 4. Stress strain curves of (a) PHB and (b) PHBV tensile bars.

4. Conclusions

The coupling of Differential Scanning Calorimetry (DSC) and tensile test allowed us to predict the melting-crystallization behavior of PHB and PHBV. Our results showed that thermal annealing treatment promoted the crystallization and segregation of PHB and PHV-domains.

The annealing-temperature-dependent multiple melting and recrystallization behavior of PHB and PHBV was studied by DSC. It was found PHB showed double melting peaks (T_{m1} and T_{m2}), after being annealed at 130˚C for 45 min. T_{m2} was not significantly influenced by annealing temperature (T_a), but the T_{m1} is T_a associated. The multiple melting phenomena were observed due to recrystallization during heating scan. It was concluded that T_a = 130˚C is a characteristic annealing temperature for PHB and PHBV. Our results showed that increasing processing temperature promoted the crystallization of PHB domains and isolation of PHV domains. For PHBV with HB:HV mole ratio of 5:1, mechanical tests performed on tensile bars showed that the thermal annealing led to a marked enhancement of the material's mechanical performance. The combination of these experiments enabled us to define a realistic processing window, in terms of thermal annealing, for both PHB and PHBV. It is crucial in the case of such thermally sensitive biopolymers displaying adequate thermal processing windows, and more attention should be thus paid to 3D printing technology, not to deteriorate their final performance.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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