



Molecular orientation in melt-spun poly(3-hydroxybutyrate) fibers: Effect of additives, drawing and stress-annealing

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ABSTRACT

Bacterial poly-3-hydroxybutyrate (P3HB) is a thermoplastic polyester with perfectly isotactic structure; it has the potential of being melt-spun to fibers, and it is thus interesting for textile applications. Aiming at developing an upscalable melt-spinning method to produce high-strength fibers, we have investigated P3HB as native polymer with the additives tri-*n*-butyl citrate (TBC) as plasticizer, and boron nitride (BN) as nucleating agent, to evaluate their effect on the melt-spinning performance of P3HB. In addition, the draw-off unit has been modified in order to enhance primary crystallization to the extent that secondary crystallization is suppressed. The such drawn fibers are dominated by longitudinally oriented lamellae rather than spherulitic structures. This allows obtaining P3HB fibers which contain domains of highly oriented molecules between crystallites, exhibiting promising tensile strengths up to 215 MPa. The wide-angle X-ray diffraction (WAXD) data suggest that besides the oriented crystalline α -phase, a highly oriented amorphous phase is present.

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1. Introduction

The use of inherently biodegradable polymers is an opportunity to reduce the amount of plastic waste that cannot be assimilated by microorganisms. Poly(3-hydroxybutyrate) (P3HB) is a sustainable and biocompatible, semi-crystalline thermoplastic polyester produced by bacteria for intracellular carbon and energy storage [1–5]. The bacteria build the polymer chains perfectly linear and isotactic, which guarantees superior properties [6–8]. Due to its biological background, P3HB is truly biodegradable in aerobic (e.g. in soil or compost) and anaerobic (e.g. in drainage pits or sea mud) conditions without forming toxic by-products [9–11]. In addition, P3HB is water insoluble, hydrophobic, and comparatively resistant to hydrolytic degradation [12–14]. Due to its exceptional properties, as well as reasonable production costs via the relatively simple biosynthesis process, P3HB is a promising substitute for conventional petrochemical plastics [15–17]. Its thermoplastic nature qualifies it for a continuous production of filaments via melt-spinning, which is arguably the most efficient process to produce fibers, and thus for the use in numerous textile and medical applications [18,19].

Bacterially synthesized P3HB possesses a glass transition temperature T_g of about 1 to 5 °C and a melting temperature T_m of about 170 to 180 °C, and it has a high tendency to crystallize, as expected for a perfectly isotactic polyester [20–22]. Primary crystallization, which includes nucleation and chain-folded lamellar crystal growth, occurs within minutes, while

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secondary crystallization, i.e. the rearrangement of molecules into energetically more favorable structures, can last for more than 100 days [23,24]. During secondary crystallization, large spherulites (spherulitic aggregates of lamellar crystals) can develop, leading to high brittleness and poor mechanical performance of native P3HB [25–28]. Moreover, its rapid thermal degradation at temperatures just above the melting temperature, variations in quality and molecular weight, and the lack of purity commonly resulting from the biotechnical production process, pose technical and scientific challenges for fiber melt-spinning [29–33].

As a result, melt-spinning of P3HB into fibers at large scale is not feasible to date. The issue has been previously addressed in the scientific literature, but just focused on the laboratory scale [17,34]. Notably, experiments performed by Iwata et al. have shown that P3HB can be spun into fibers with tensile strengths exceeding 1 GPa [35,36]. These authors spun ultra-high molecular weight P3HB ($M_w > 3.7$ MDa) into ice water to allow only small crystals to grow during isothermal crystallization below T_g , followed by a mechanical orientation of the free molecular chains between the crystal nuclei through stretching [35,36]. Applying similar techniques on P3HB with $M_w < 750$ kDa, the highest tensile strength achieved was 740 MPa [35], but the methods used are complex and cannot readily be transferred into an industrial process. P3HB fibers were also manufactured by conventional melt-spinning at laboratory scale, applying special finishes and uncommon procedures, but owing to the degradation of P3HB during extrusion, the tensile strength of these fibers did not exceed 500 MPa [27,37].

P3HB crystallization plays an important role during the melt-spinning process. The nucleation step in the crystalline growth process is generally associated with the presence of inhomogeneities or foreign particles in the melt [38,39]. In the case of P3HB, nucleating agents may be helpful to increase crystallization rate, and to decrease the dimension of unwanted spherulites [22,40]. Common nucleating agents are non-soluble inorganic fillers like metal oxides, metal salts, silicates or boron nitride with particle sizes of about 3 μm [17,41]. For the present study, boron nitride (BN) was chosen since it is one of the best nucleating agents reported for P3HB [22,42–44]. The inherent brittleness of native P3HB can be overcome by adding plasticizers [45–47]. To maintain biodegradability, non-toxic citrate plasticizers derived from naturally occurring citric acid are favored for this purpose [47]. Thus, tri-*n*-butyl citrate (TBC) was chosen as plasticizer in the present study.

The aim of this work was to develop an upscalable melt-spinning method for high-strength P3HB fibers by studying the effects of industrially manageable additives and various filament drawing setups on fiber performance. The additives were analyzed either in combination with P3HB powder extracted from bacteria or using pellets extruded from native polymer powder. In order to address the poor melt strength and the particular crystallization behavior of P3HB, the godet set-up of our draw-off unit was modified. Finally, the physical and structural properties of the produced filaments were characterized and compared to those of conventional fibers.

2. Experimental section

2.1. Materials

Different base materials were considered in this work (see Table 1). Biomer P209 (P3HB with nucleating agent and plasticizers) and Biomer P309 (P3HB with nucleating agent, without plasticizers), both manufactured via melt-mixing and pelletizing, were provided by Biomer (Krailling, Germany). The density was 1.2 g/cm³, the melting temperature T_m was 168 °C (P209) and 180 °C (P309), and the mass average molar mass M_w was 0.5 MDa (P209) and 0.6 MDa (P309), respectively. For reference purposes, Biomer also provided the raw polymer (T19) extracted from bacteria, which they used to produce the supplied compounds P209 and P309. The raw polymer T19 comes as powder with a M_w of 1.6 MDa. The polymer was identified by GC as pure P3HB homopolymer without hydroxyvalerate content. Plasticizer tri-*n*-butyl citrate (TBC) with the trade name Citrofol BI was provided by Jungbunzlauer (Ladenburg, Germany). Nucleating agent boron nitride (BN) was provided as well by Biomer. Moreover, a powdery mixture of the raw polymer T19 with 20 wt% of the plasticizer TBC was prepared in-house by mechanical mixing to a sample labeled as T19+.

2.2. Melt spinning and annealing

Fiber melt-spinning was carried out on a customized pilot melt-spinning plant originally built by Fourné Polymertechnik (Alfter-Impekoven, Germany). This pilot plant – having features corresponding to an industrial plant – enables the prototype production of multicomponent fibers with various cross-sections and material combinations with a throughput of

Table 1

Base materials considered in this study. Type and composition of the low molecular weight polymeric processing aids were not disclosed by the provider.

Label	Produced from	Plasticizer (TBC)	Nucleating agent (BN)	Processing aids (not specified)	Preparation	Appearance
T19	(raw polymer)	–	–	–	–	Powder
T19+	T19	20 wt%	–	–	Mixing	Powder
P209	T19	20 wt%	0.5 wt%	Approx. 10 wt%	Extrusion	Pellets
P309	T19	–	0.5 wt%	–	Extrusion	Pellets

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