Effect of Stress and Temperature on the Molecular Orientation of Melt-spun Poly(3-hydroxybutyrate) Fibers

Rudolf Hufenus, Felix A. Reifler
Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland
rudolf.hufenus@empa.ch

OBJECTIVE

In a previous work we presented the successful spinning of poly(3-hydroxybutyrate) (P3HB) fibers applying an upscalable melt-drawing method [1, 2]. This work aims to an understanding of the effect of stress and temperature on the molecular orientation of melt-spun P3HB fibers. To this end, the physical and structural properties of the produced filaments are characterized applying wide angle X-ray diffraction (WAXD) in combination with tensile and heating stages.

INTRODUCTION

The use of inherently biodegradable polymers is an opportunity to reduce the amount of plastic waste that cannot be assimilated by microorganisms. P3HB is a sustainable and biocompatible, semi-crystalline thermoplastic polyester produced by bacteria for intracellular carbon and energy storage [3]. The bacteria build the polymer chains perfectly linear and isotactic, which guarantees superior properties [4]. 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 [5]. In addition, P3HB is water insoluble, hydrophobic, and comparatively resistant to hydrolytic degradation [6]. 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 [7]. 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 [8].

However, its rapid thermal degradation at temperatures just above the melting temperature, and the brittleness of native P3HB, pose technical and scientific challenges [9]. Other difficulties for industrial transfer include the raw polymer impurity, varying viscosity, broad molecular weight distribution, and complex crystallization behavior [10]. As these are inherent weaknesses of P3HB processed from natural resources, we proposed the use of additives to improve its melt-spinnability [1]. On one hand we proved that nucleating agents control and stabilize crystallization, on the other hand we showed how plasticizers damp viscosity fluctuations and enable a decrease of processing temperatures, resulting in reduced thermal degradation (loss of molecular weight). In addition to the incorporation of additives, we installed an intermediate godet in the draw-off unit to address the poor melt strength and the complex crystallization behavior of P3HB. By introducing the intermediate godet, we accomplished an oriented crystallization before complete solidification. Thus the extrudate could withstand the drawing forces induced by melt-spinning, and filaments dominated by longitudinally oriented lamellae rather than spherulitic structures were obtained. Secondary crystallization could be suppressed, which otherwise would lead to brittleness and poor mechanical performance.

In the equatorial 2Theta scan of the WAXD patterns, we observed a series of local maxima. We postulated a highly ordered amorphous phase, which is kinetically trapped between the aligned lamellae of the crystalline α-phase [1]. This is in contrast to the previous literature, where diffraction signals in this region are commonly described as one reflection, assigned to the so-called "β-form" of P3HB. In our model, the local maxima in the 2Theta scan correspond to preferred distances between polymer chains that are oriented nearly parallel to, but irregularly arranged along the fiber direction.

For the present study, P3HB fibers are subjected to various tensions and temperatures while tracing their structural response by *in-situ* WAXD.

EXPERIMENTAL APPROACH

Fiber melt-spinning of P3HB (Biomer P209, Biomer, Krailling, Germany) was carried out on Empa's custom-made pilot melt-spinning plant [10]. The analytical tools applied included wide angle X-ray diffraction (WAXD), recorded on a Bruker Nanostar U diffractometer (Bruker AXS, Karlsruhe, Germany) with $Cu_{K\alpha 1}$ radiation.

RESULTS AND DISCUSSION

From the WAXD pattern of fully drawn P3HB fibers under tension (Fig. 1) it can be seen that the intensities of the highly oriented crystalline reflections (020) and (110) decrease with increasing tension.

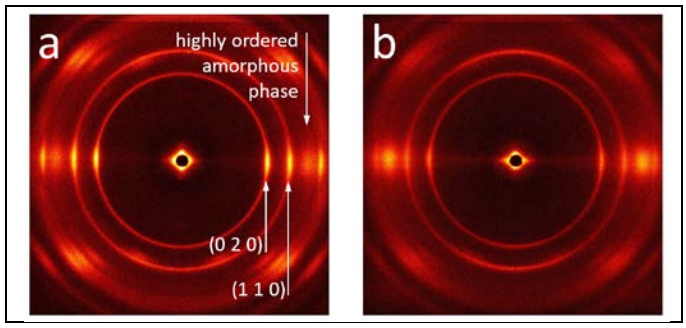

Figure 1: WAXD pattern of a P3HB fiber under tension. (a) 0 N (0 MPa, strain 0 %); (b) 1.05 N (165 MPa, strain 59 %).

Since the total intensity of the (020) reflection (including the reflections of the poorly oriented crystallites on the whole

ring) remains constant, this intensity drop can be explained by a reduction in highly oriented crystalline lamellae, i.e. by a smaller relative amount of highly oriented crystals. Simultaneously, the intensity of the reflections assigned to the highly ordered amorphous phase is considerably increasing.

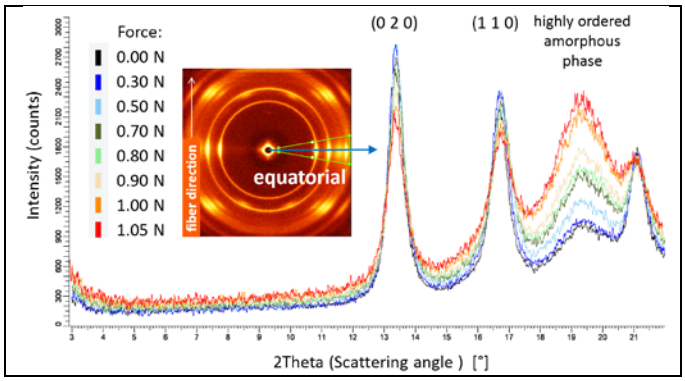

Figure 2: Structural response of the P3HB fiber in Fig. 1 to increasing tensional forces: 2Theta scan of the equatorial sector indicated by the green wedge cursor in the WAXD pattern.

2Theta scans of the equatorial sectors in WAXD patterns recorded under increasing tensional forces (Fig. 2) show this behavior in a more detailed way: enhanced orientation of the amorphous phase is realized to the disadvantage of the orientation of the crystalline phase. While the orientation of the amorphous polymer chains between the shish-kebab structures within the fiber is increasing, these chains can enforce a tilting of some of the crystalline lamellae, which in turn results in local bending of the shish. From the literature it is known that the shish have a certain flexibility [11].

The evaluation of WAXD patterns recorded under a cyclic change of load reveals a high degree of reversibility for these phenomena. Thus, the proposed bending of the shish-kebab structure is partly reversible, depending on the external load. The detected reversibility also supports our model of the highly ordered amorphous phase described in the introduction.

Annealing under tension remarkably increases the orientation of the crystalline phase: annealing at a temperature of 110 °C with a static load of 25 grams (equal to 25 % of the ultimate tensile strength of the fiber) increases the amount of highly oriented lamellae from 21 % to 50 %. At the same time, the ultimate tensile strength increases from 163 MPa to 189 MPa.

CONCLUSION

WAXD data of our P3HB fibers suggest that besides the oriented and unoriented crystalline lamellae dominating the fiber structure, a highly oriented amorphous phase is present in the fibers. Under load, the orientation of the amorphous phase is enhanced, to the disadvantage of the orientation in the crystalline phase. Cyclic drawing experiments with simultaneous WAXD support this model.

KEYWORDS

Melt-spinning; biopolyester; biopolymer; wide-angle X-ray diffraction

ACKNOWLEDGMENT

The authors thank Urs J. Hänggi from Biomer (Krailling, Germany) for providing material, and Benno Wüst for operating the spinning plant.

REFERENCES

1. Hufenus, R., et al. “Molecular orientation in melt-spun poly(3-hydroxybutyrate) fibers: effect of additives, drawing and stress-annealing.” *European Polymer Journal*, 2015, 71: 12-26.
2. Hufenus, R., F.A. Reifler, M.P. Fernández-Ronco. “Molecular orientation in melt-spun P3HB fibers.” *The Fiber Society Spring Conference Proceedings*, 2015, Shanghai, China.
3. Sudesh, K., H. Abe, Y. Doi. “Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters.” *Progress in Polymer Science*, 2000, 25(10): 1503-55.
4. Pan, P., Y. Inoue. “Polymorphism and isomorphism in biodegradable polyesters” *Progress in Polymer Science*, 2009, 34(7): 605-40.
5. Bonartseva, G.A., et al. “Aerobic and anaerobic microbial degradation of poly-β-hydroxybutyrate produced by Azotobacter chroococcum.” *Applied Biochemistry and Biotechnology-Part A Enzyme Engineering and Biotechnology*, 2003, 109(1-3): 285-301.
6. Zinn, M., R. Hany. “Tailored material properties of polyhydroxyalkanoates through biosynthesis and chemical modification.” *Advanced Engineering Materials*, 2005, 7(5): 408-11.
7. Laycock, B., et al. “The chemomechanical properties of microbial polyhydroxyalkanoates.” *Progress in Polymer Science*, 2013, 38(3-4): 536-83.
8. Ziabicki, A. *Fundamentals of Fibre Formation*. London: John Wiley & Sons, Ltd., 1976.
9. Barham, P.J., A. Keller. “Relationship between microstructure and mode of fracture in polyhydroxybutyrate.” *Journal of Polymer Science. Part A-2, Polymer Physics*, 1986, 24(1): 69-77.
10. Hufenus, R., et al. “Biodegradable Bicomponent Fibers from Renewable Sources: Melt-Spinning of Poly(lactic acid) and Poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)].” *Macromolecular Materials and Engineering*, 2012, 297(1): 75-84.
11. Keller, A., H.W.H. Kolnaar. “Flow-Induced Orientation and Structure Formation.” *Materials Science and Technology*, 2006, Wiley-VCH Verlag GmbH & Co. KGaA.