Processing of Gel-Spun Poly(β-hydroxybutyrate) Fibers

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ABSTRACT: Poly(β-hydroxybutyrate) (PHB) is a bacteria storage biodegradable polyester that is considered to be a natural substitute for synthetic thermoplastics in many applications. However, brittleness hampers its utility. This study shows that oriented elastic fibers of PHB with favorable mechanical properties (360-MPa tensile strength and 5.6-GPa Young's modulus) can be produced by the spinning and drawing of a concentrated PHB gel using a three-stage fiber processing technique. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2260–2264, 2001

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INTRODUCTION

Poly(β-hydroxybutyrate) (PHB) is the main member of the poly(hydroxyalconates) family of biodegradable polyesters, which are considered to be natural substitutes for synthetic thermoplastics in many applications. Among the many useful properties of PHB are biodegradability and biocompatibility. These combined with ease of synthesis are of great practical interest. However, there are relatively few studies of processing methods to fabricate PHB-based materials with mechanical characteristics suitable for practical applications.[1,2]

It is now well known that PHB suffers from several processing problems. One of them is that when cooled from the melt, the PHB homopolymer tends to crystallize slowly from relatively few nucleation centers, which, given time, results in the formation of large crystallites. This microstructure causes brittleness in the material.[3,4]

Another processing problem is that the PHB melt is unstable and quickly degrades at temperatures just above the melting point.[5] Despite the low thermostability, PHB can be injection molded and extruded if care is taken to minimize the processing temperature and residence time.[1,2] Further improvements in behavior can be provided by adding plasticizers and nucleating agents to counteract the brittleness. Also, the ductility of the fabricated material can be enhanced by annealing at an elevated temperature.[4] Notwithstanding these measures, PHB samples still tend to exhibit coarse crystallinity, brittleness, and poor mechanical performance. In fact, PHB is typically regarded as having a tensile strength of about 40 MPa and a Young's modulus of around 3–4 GPa.[6,7]

Recently, members of our group found a means to produce PHB fibers with improved tensile strength (190 MPa) and Young's modulus (5.6 GPa).[8] This involved melt extrusion, hot drawing, and elevated temperature annealing of the PHB fibers. The most essential factor was immediate postextrusion stretching of the melt. This preconditioning step, which may suppress large crystal

growth during cooling, resulted in enduring drawability via necking, even at room temperature.

A possible explanation for the effect of preconditioning relates to the crystallization behavior of the extruded filament. The stress applied to the melt during extrusion may suppress the growth of large crystallites, which relates to the relatively weak interfaces responsible for sample brittleness. The deformation of the PHB fibers via neck formation during subsequent drawing suggests transformation of residual lamellar crystallites to fibrillar ones. A final degree of fibrillar structure perfection and orientation was achieved when the stretched sample was annealed. By establishing a means to change the crystallization behavior of the PHB melt, sample brittleness was eliminated.

In the present work the remaining problem of thermal stability was addressed by employing gel-spun technology,[9] which can reduce the processing temperature. This approach was used in the past to spin ultrahigh molecular weight polymers where polymer chain entanglement precluded melt spinning.

EXPERIMENTAL

A homopolymer PHB powder was supplied by Prof. T. G. Volova (Institute of Biophysics, Krasnoyarsk, Russia). It was synthesized by continuous fermentation of *Alcaligenes eutrophus*.[10] The weight-average molecular weight (M_w) was determined from intrinsic viscosity measurements using an Ubbelohde-type dilution viscometer and Mark–Houwink–Sakurada equation parameters calculated earlier.[5] The PHB sample used in this work had a M_w of 3×10^5 g/mol.

The polymer was purified before spinning by the filtration of a dilute solution in chloroform to eliminate contaminants and high molecular weight inclusions. Among several solvents, 1,2-dichloroethane (DCE) was found to be the best to prepare a gel of PHB suitable for extrusion. A solution of PHB in DCE of the highest possible concentration, which turned out to be 20 wt %, was prepared by stirring at about 80°C. Then part of the solvent was allowed to evaporate during several hours at room temperature to form a solid gel with a PHB content of 30–32 wt %.

The process employed and described here for spinning PHB gel fibers involved three main production stages as identified in the previous PHB melt spinning study[8]: extrusion with a precondi-

tioning stretch, hot drawing of the fiber, and final annealing.

Stage 1: Extrusion and Preconditioning Stretch

The gel was extruded using an Instron capillary rheometer (capillary length/diameter ratio of 20) at 170°C. The processing temperature was 10°C below the polymer melting point of 180°C, which was determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min. To stretch the material coming out of the die, the extrudate was collected on a speed controlled drum. Combining the extrusion and winding rates allowed the samples to be produced at different preconditioning draw ratios (PDR). The PDR of the fiber was determined from the ratio of the linear density of the stretched fiber to the linear density of the fiber spun without stretch. It was established in the previous melt-spun trials[8] that a PDR of about 2 is optimal for further drawing, and this ratio was adopted here.

Stage 2: Hot Drawing

The next stage was continuous hot drawing of the preconditioned extrudate between two rollers at 120°C to a total draw ratio (DR) of about 10.

Stage 3: Annealing

Finally, samples were stretched at room temperature to 180% of their initial length in an Instron-1121 tensile testing machine. They were fixed in position and then annealed at 150°C for 1 h.

The effect of each of the three stages was studied by analyzing samples of the corresponding fibers from each step. The tensile properties were studied using the Instron-1121 machine, and the dynamic modulus and loss factor were determined at a frequency of 30 Hz using a Polymer Laboratory DMTA instrument.

RESULTS AND DISCUSSION

The as-spun fibers from stage 1 were tested for their mechanical properties. As in the melt-spinning study,[8] tensile tests showed that the fibers could be drawn via a necking process both at and above room temperature. The necking, which corresponds to the stress–strain yield point, occurred at an applied strain of 6–7%. At ambient condi-
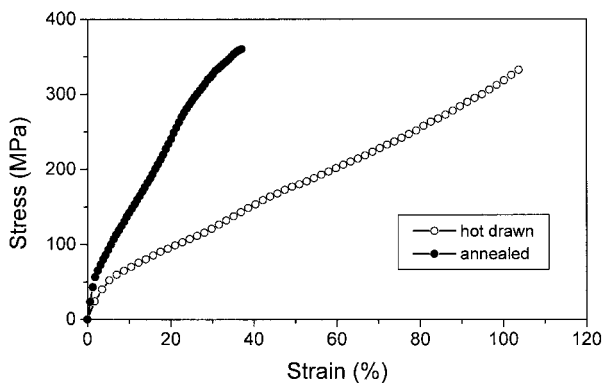
Figure 1 The stress–strain curves of the drawn and annealed samples at room temperature.

tions the tensile behavior was typical of most conventional semicrystalline polymers.

The temperature dependence of the drawability of the as-spun fibers was then studied over a range of 20–160°C. The maximum draw ratio (DR) of about 5 was obtained at 120°C. It is also worth noting that the amenability of the preconditioned fibers to subsequent hot drawing was maintained for at least several months. Moreover, the drawn material was rubberlike. Achieving this behavior was striking because extruded PHB has a reputation for being brittle.

Figure 1 shows the room temperature tensile behavior of the gel-spun fibers after stage 2 (hot drawn but not annealed) and after stage 3 (annealed). The stress–strain curves obtained were typical of highly oriented semicrystalline polymers and similar to those of the corresponding melt-spun fiber.[8] However, the tensile strength of both the gel-spun fiber types (after stages 2 and 3) was about double that of their melt-spun counterparts. Both gel-spun fiber types also exhibited exceptional rubberlike behavior and a high degree of elastic recovery.

A comparison of the nonannealed and annealed gel-spun fibers revealed that the annealing procedure improved only the stiffness of the hot-

drawn fiber and the tensile strength was unchanged. Table I summarizes the tensile behavior of fibers from all three gel spinning stages.

A comparison of the PHB gel-spun and melt-spun final products showed that the tensile strength of the gel-spun material was much improved (360 vs. 190 MPa) while the tensile modulus was unchanged (5.6 GPa). The lowering of the processing temperature in the gel-spinning process (10°C below the melting point) may reduce the thermal degradation of polymer chains without influencing structure formation. This was verified by DSC and wide angle X-ray spectroscopy (WAXS) measurements that showed no discernible differences in the crystalline structure between the melt- and gel-spun oriented samples. The DSC data showed degrees of crystallinity of 67 and 69% for the melt-spun and gel-spun oriented samples, respectively, and no difference in the melting peak position (177°C). As expected, the WAXS measurements revealed higher values of crystallinity than the DSC. However, the values for the melt- and gel-spun oriented samples were again similar at 72 and 75%, respectively. Also, no changes in crystal dimensions were observed in the WAXS tests. Observations by other workers showed that a fraction of pseudohexagonal crystals with different crystal unit cell parameters may exist in highly oriented melt-spun PHB.[11–13] However, no correlation between the processing conditions and the appearance of such crystal modifications was mentioned.

The dynamic modulus (E') and loss factor (tan δ) for all three gel-spun fiber types (stages 1–3) are shown in Figures 2 and 3 for a heating run from $-80°C$ up to the melting region of each sample. The dynamic mechanical measurements showed that both the drawing and annealing resulted in an improvement in the mechanical properties of the samples. As expected, the dynamic modulus of all samples at room temperature generally became larger than the corresponding static moduli calculated from the strain–stress

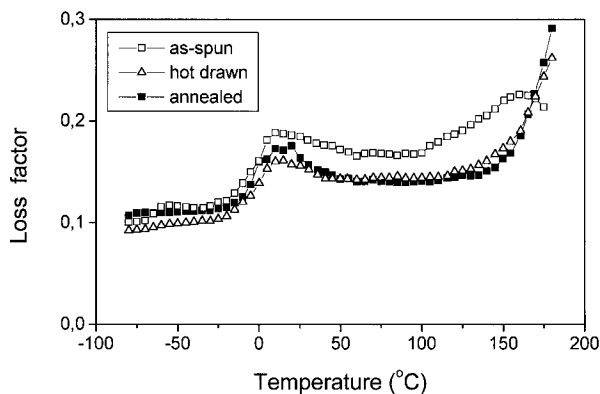**Table I   Tensile Properties of Gel-Spun Samples at Room Temperature**

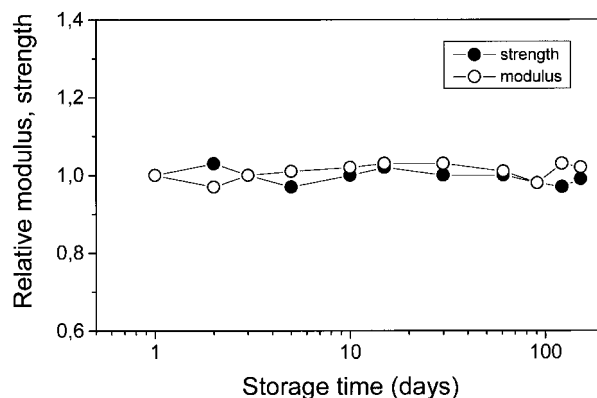| Sample	Tensile Strength (MPa)	Static Modulus (GPa)	Dynamic Modulus (GPa)	Strain at Break (%)
As spun (PDR = 2)	103	2.0	4.6	250
Hot drawn (DR = 10)	332	3.8	5.8	104
Annealed	360	5.6	7.5	37
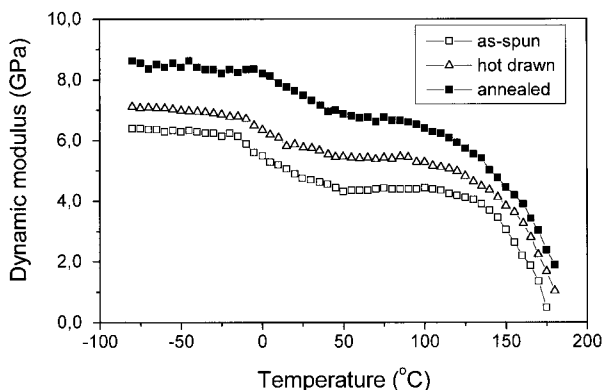
Figure 2 The dynamic mechanical modulus as a function of temperature for the as-spun, drawn, and annealed samples.

Figure 4 The relative tensile strength and modulus as functions of the storage time for the annealed sample.

curves (tensile moduli, Table I). The difference was caused by different measuring methods because dynamic modulus measurements are usually performed at low applied strain (in the linear viscoelasticity region); hence, the influence of the relaxation processes in the polymer was diminished. The experimental values of the dynamic modulus obtained here were in good agreement with theoretical predictions published elsewhere.[14]

It was shown previously[15] that loss factor curves in PHB may show three dispersion peaks (α, β, and γ) descending from higher temperatures. It is recognized that the α process in polymers corresponds to the onset of chain mobility accompanying the crystalline melting process, and the β peak is primarily a dispersion peak reflecting segmental motion of molecular chains in the amorphous regions (i.e., the α and β peaks correspond to the softening and glass-transition

temperatures, respectively). The γ peak is caused by the local mode relaxation of cooperative motions in methyl or ester groups.

The α peak for preconditioned gel-spun fibers (after stage 1, Fig. 3) was found to occur at 160°C; however, the tan δ values started to rise at about 110°C, which was consistent with relatively high sample drawability at temperatures above that. For the final annealed fibers (after stage 3) the α-peak temperature in the loss factor curve was almost indistinguishable from the melting region. This behavior was consistent with the impossibility of further stretching at any temperature.

The β peak of the preconditioned fibers occurred at 5°C. The temperature at which the β peak appeared was higher for the hot-drawn fibers and higher still for the final annealed material. In addition, the higher the peak appearance temperature, the lower the peak area.

A faint γ peak was detected in the preconditioned fibers at −60°C, and it disappeared in the hot-drawn and annealed samples. This implies that the molecular motion of the methyl or ester groups was restricted in the drawn material, which is consistent with a more compact structure and indicative of greater molecular orientation.

The tensile properties were determined for the hot-drawn and annealed PHB gel-spun fibers over a 6-month storage period under ambient conditions (Figs. 4, 5). The tensile strength and modulus values were normalized by the corresponding properties measured immediately after processing. Figure 4 reveals no appreciable aging effect for the final annealed fibers. However, Figure 5 shows an increase in stiffness and a decrease in strength over time for the hot-drawn fibers.

Figure 3 The loss factor as a function of temperature for the as-spun, drawn, and annealed samples.
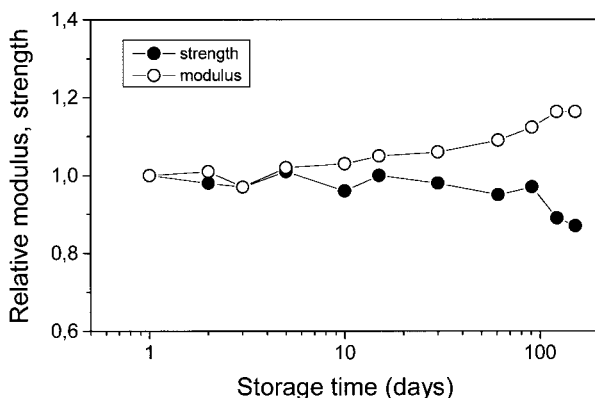
Figure 5 The relative tensile strength and modulus as functions of the storage time for the drawn sample.

However, it should be mentioned that the aging effects in the hot-drawn fibers may also relate to residual solvent, which was previously experienced in highly oriented gel-spun fibers of ultra-high molecular weight polyethylene.[16]

CONCLUSIONS

Elastic fibers of PHB with a tensile strength and Young's modulus up to 360 MPa and 5.6 GPa, respectively, can be produced by the spinning and drawing of a concentrated PHB gel using a three-stage fiber processing technique.

The tensile strength was improved in comparison to a PHB melt-spun material, and this can be attributed to a lower polymer thermal degradation by the reduction in the spinning temperature.

Further work is needed to better understand the formation of oriented PHB fibers. This would assist in the optimization of the various process-ing stages to further enhance PHB fiber properties.

REFERENCES

1. Tormala, P.; Rokkanen, P.; Vainionpaa, S.; Laiho, J.; Heponen, V.-P.; Pohjonen, T. U.S. Pat. Applic. 4,968,317, 1990.
2. Wang, Y. D.; Yamamoto, T.; Cakmak, M. J Appl Polym Sci 1996, 61, 1957.
3. Doyle, C.; Tanner, E. T.; Bonfield, W. Biomaterials 1991, 12, 841.
4. de Koning, G. J. M.; Lemstra, P. J. Polymer 1993, 34, 4089.
5. Marchessault, R. H.; Okamura, K.; Su, C. J. Macromolecules 1970, 3, 735.
6. Barham, P. J.; Organ, S. J. J Mater Sci 1994, 29, 1676.
7. de Koning, G. J. M.; Scheeren, A. H. C.; Lemstra, P. J.; Peeters, M.; Reynaers, H. Polymer 1994, 35, 4598.
8. Gordeyev, S. A.; Nekrasov, Y. P. J Mater Sci Lett 1999, 18, 1691.
9. Smith, P.; Lemstra, P. J. J Mater Sci 1980, 15, 505.
10. (a) Volova, T. G.; Kalacheva, G. Rus. Pat. 2,051,967, 1996; (b) Volova, T. G.; Kalacheva, G. Bull Invent 1996, 1.
11. Orts, W. J.; Marchessault, R. H.; Bluhm, T. L.; Hamer, G. K. Macromolecules 1990, 23, 5368.
12. Furuhashi, Y.; Ito, H.; Kikutani, T.; Yamamoto, T.; Kimizu, M.; Cakmak, M. J Polym Sci Part B Polym Phys 1998, 36, 2471.
13. Schmack, G.; Jehnichen, D.; Vogel, R.; Tandler, B. J Polym Sci Part B Polym Phys 2000, 38, 2841.
14. Nicholson, T. M.; Unwin, A. P.; Ward, I. M.; Siripittayananon, J.; Wongchanapiboon, T. J Chem Soc Faraday Trans 1995, 91, 2623.
15. Mitomo, H.; Barham, P. J.; Keller, A. Polym Commun 1988, 29, 112.
16. Alekseev, V. G.; Gordeev, S. A.; Pakhomov, P. M. Fiber Chem 1995, 27, 41.