Orientation Effect in Poly (butylene succinate) Fibers

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SUMMARY

Fibers of poly (butylene succinate) (PBS) were prepared using a single screw extruder at various take-up speeds. Changes in fiber structure, morphology and physical properties were investigated using sonic velocity measurements and X-ray diffraction. High take up speeds enhanced some of the properties of PBS fibers as a consequence of changes in molecular orientation and crystallinity. Spherulites of PBS were also obtained at 90°C.

INTRODUCTION

The increase in production of plastics materials and plastics waste has stimulated studies of new biodegradable synthetic polymers. Many aliphatic polyesters such as poly (butylene succinate) (PBS) and their blends have been reported to be biodegradable under appropriate conditions [1, 2, 3]. Microorganisms such as fungi, actinomycetes and bacteria can biodegrade PBS[4]. Morphological changes in PBS single crystal lamellae, induced by hydrolysis, have been investigated to explain biodegradation. It was found that the edge regions of single crystal lamellae can be affected by hydrolysis. Cracks on the surface of spherulites after hydrolysis are a consequence of molecular arrangement in the crystallographic unit cell[5]. Ihn et al found that PBS molecules are packed perpendicular to the basal plane of the single crystals, and twin crystals with a (110) twin plane were found. Lattice parameters of the PBS crystal in the monoclinic unit cell in a single crystals are a = 0.523 nm, b = 0.908 nm, c = 1.079 nm, and beta = 123.87 degrees.

In this work, to produce changes in molecular orientation and crystallinity in PBS fibers, a single screw extruder was used to obtain PBS fibers at different take-up speeds. We obtained a value for the sonic modulus, some X-ray diffraction patterns, and WAXD intensity profiles from equatorial and meridian samples. Spherulite morphologies were studied by means of a polarizing optical microscope. Finally, we obtained lattice parameters in the monoclinic unit cell (a and b) from fiber samples.

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EXPERIMENTAL

Materials

PBS was synthesized by reacting dimethylsuccinate and 1,4-butanediol, in the presence of titanium tetraisopropoxide in a nitrogen atmosphere at 160-200 °C. A round bottomed stainless steel reactor was equipped with a mechanical stirrer, thermocouple and a product outlet nozzle for pelletizing. For comparison, we also used commercial PBS, Bionelle 1000 (Showa Kobunshi Ltd., Japan).

Fiber processing

PBS fibers were obtained from pellets using a single-screw extruder (LABO PLASTOMILL, Toyoseiki Co) with a T-die (50 mm in width and 2 mm in thickness) at a screw rotation speed of 10 rpm. Take-up speeds of 10, 20, 30 and 60 m/min were used. The temperature of the chill roller was 50°C. The extrusion temperature profile in the barrel zones was set from hopper to die at 100, 120, 130 and 130°C (The last one was the die temperature). PBS pellets were dried overnight under vacuum at 80°C, and then placed in a dry oven at 50°C prior to use.

Preparation of spherulites

Sheets of PBS were melted between two glass slides at 160 °C for 30 minutes. Then, the samples were cooled at 90 °C for 60 minutes. Spherulite morphologies were studied by a polarizing optical microscope (Olympus BX 50).

Characterization

Sonic velocity modulus was evaluated using a sonic propagation method at room temperature, with a pulse propagation meter, Rheovibron DDV-5-B (Orientec Co.). The pulse frequency was 10 KHz and the pulse propagation distance between sending and receiving the sonic pulse was 250-300 mm. In some cases, it was in 100-150 mm. The sonic modulus ($E_s = c^2\rho$), was calculated from the sonic velocity c and the density ρ. The slope of a plot of time against length is c. The value of ρ was obtained by density gradient column method.

WAXD (wide-angle X-ray diffraction) diagrams of samples were recorded using CuKα radiation with RAD-C (Rigaku Denki Co). The X-ray generator was operated at 40 KV and 35 mA for 40 minutes. WAXD photographs were taken on a flat film, giving WAXD equatorial and meridian scans of intensity profiles, too.

RESULTS AND DISCUSSION

Figure 1 shows the results obtained from sonic modulus measurements on fibers of PBS as a function of the take-up speed of the extruder. The sonic modulus obtained at a speed of 10 m/min in commercial PBS fiber was 0.83 GPa. The value for the non-commercial PBS fibers obtained at the same take-up speed was slightly higher. The sonic modulus decreased when the take-up speed of the extruder was increased to 20, 30 and 60 m/min. At 60 m/min, the sonic modulus was just a little higher than for samples produced at 20 and 30 m/min in response to the changes in molecular orientation and crystallinity.

In **Figures 2A to 2E** are shown the WAXD patterns of PBS fiber samples obtained in the draw direction. From 2A to 2D, it was not possible to detect a substantial difference between WAXD patterns. All of them showed related patterns with no molecular orientation. Differences in WAXD patterns became more evident in sample 2E. This showed a pattern associated with molecular orientation samples and crystallinity. It was consistent with the sonic modulus results mentioned above.

Results from WAXD equatorial and meridian scan intensity profiles of PBS fibers are shown in **Figures 3 and 4**. In the WAXD equatorial profile there are three peaks. A big peak was indexed as (110), a second small peak was indexed as (020). The last one was almost unnoticeable in samples at 60 m/min take-up speed. It was possible to observe a third peak, associated with the index (120). In some cases, it was undetectable. It was possible to observe only two peaks in the WAXD meridian profile. As with the WAXD equatorial scan intensity profiles, there was a big peak indexed as (110). The second peak was not so tiny; it was indexed as (020).

By comparing WAXD equatorial scan intensity profiles with WAXD meridian scan intensity profiles of PBS fibers it is possible to establish the effect of high take-up speed extrusion. Thus, molecular

Figure 1 Sonic modulus from PBS fibers

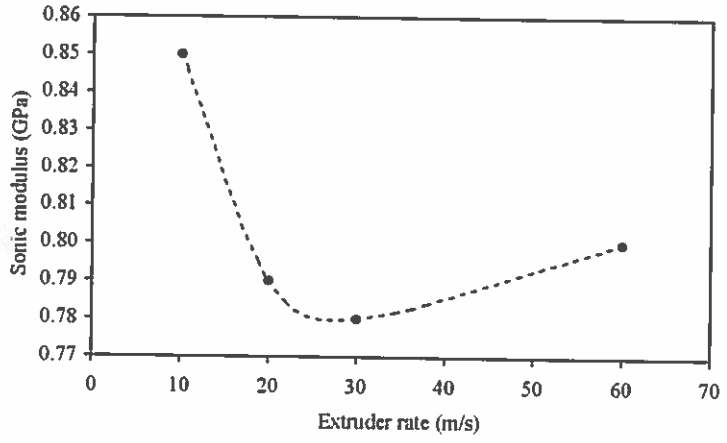


Figure 2 WAXD patterns of PBS fibers at various take-up speeds. (a) Bionelle at 10 m/min (b) PBS at 10 m/min (c) PBS at 20 m/min, (d) PBS at 30 m/min and (e) PBS at 60 m/min. Drawing direction is vertical.

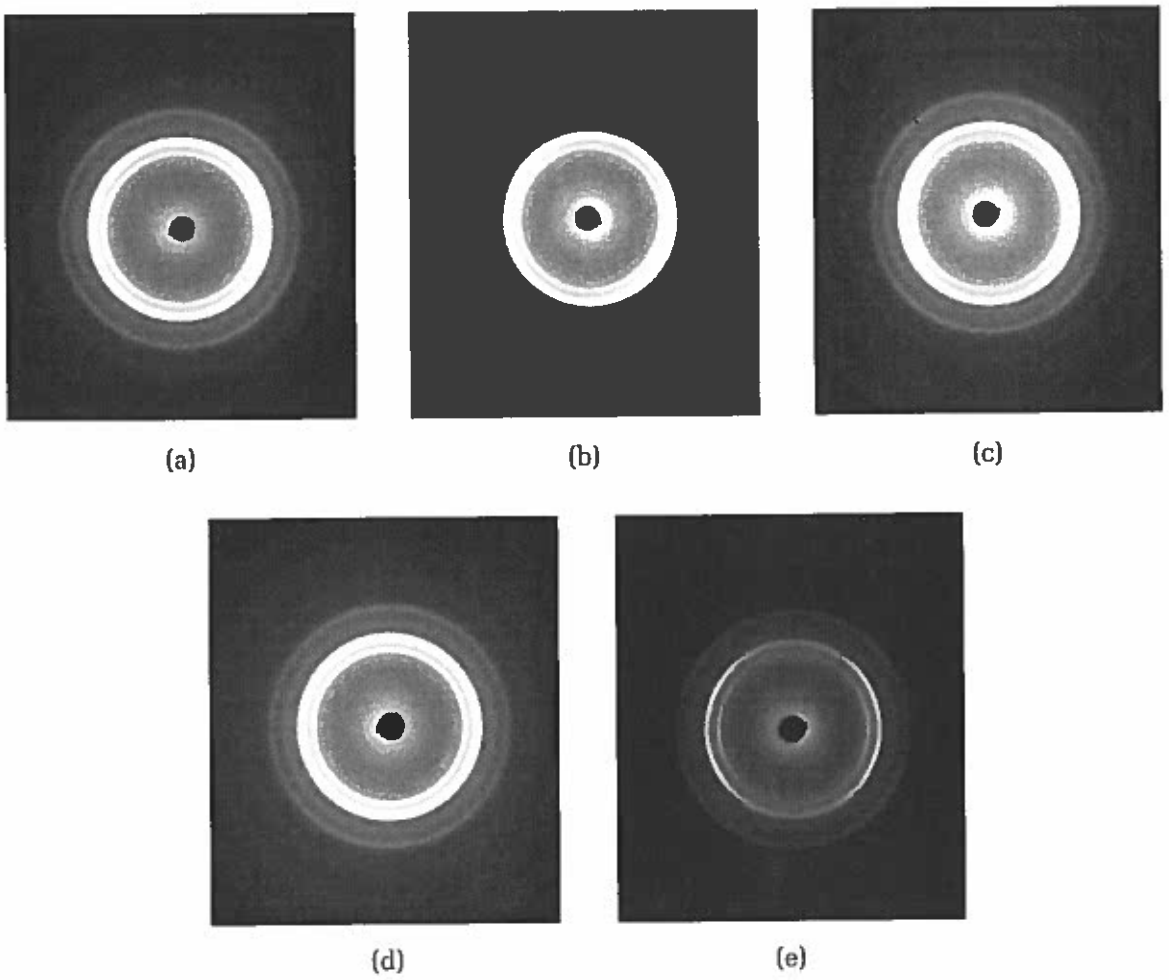


Figure 3 WAXD equatorials scan intensity profiles of PBS fibers obtained using various take up speeds. From top to bottom: 10 m/min for the commercial Bionelle sample and 10, 20, 30 and 60 m/min for non-commercial PBS

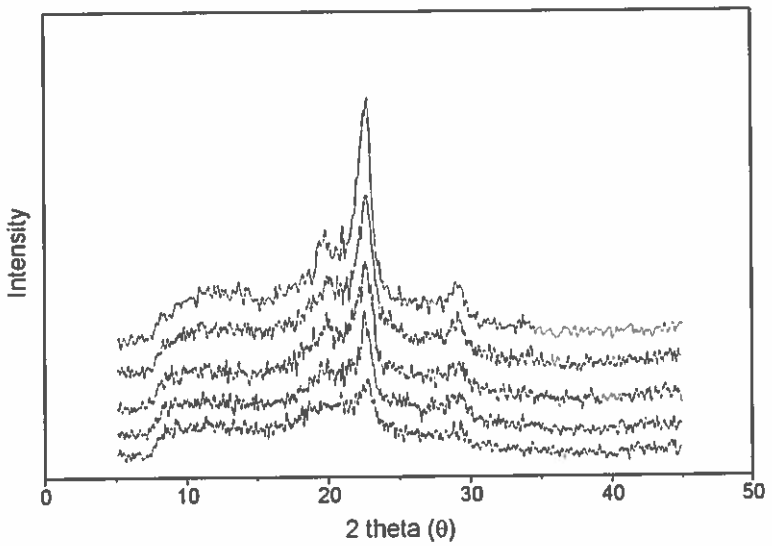


Figure 4 WAXD meridian scan intensity profiles of PBS fibers obtained using various take up speeds. From top to bottom: 10 m/min for the commercial Bionelle sample and 10, 20, 30 and 60 m/min for no-commercial PBS

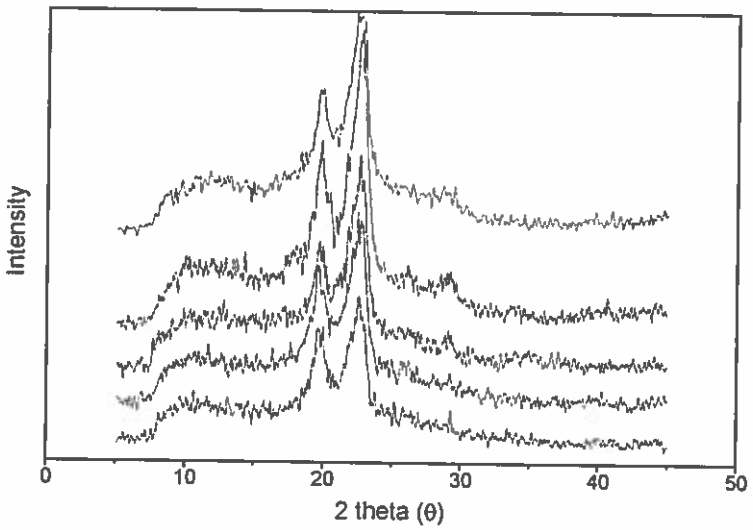
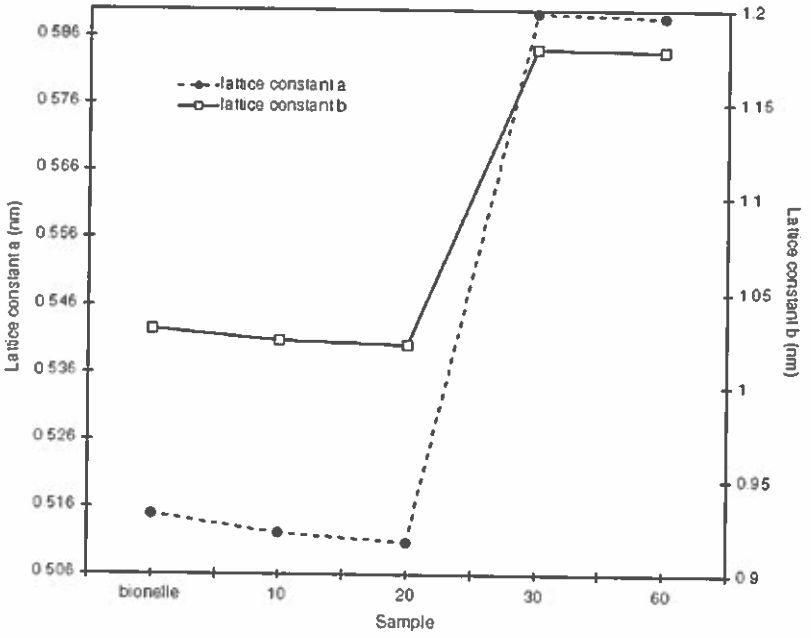


Figure 5 Lattice constants (a and b) from WAXD meridian scan intensity profiles of PBS fibers obtained using various take-up speeds



orientation is induced in a major or minor degree by the extrusion process when the take-up speed is increased sufficiently.

Qualitatively, as with the commercial PBS, the non-commercial fiber samples obtained at 10 m/min take-up speed showed a certain molecular orientation and crystallinity degree but it was too small to detect in the WAXD patterns. Samples extruded at 20 and 30 m/min showed little change in their WAXD intensity profiles as a result of changes in molecular orientation during extrusion. More pronounced differences were obtained in samples drawn at 60 m/min.

Figures 5 and 6 show the lattice constants (a and b) obtained from WAXD meridian and equatorial scan

Figure 6 Lattice constants (a and b) from WAXD equatorial scan intensity profiles of PBS fibers obtained using various take-up speeds

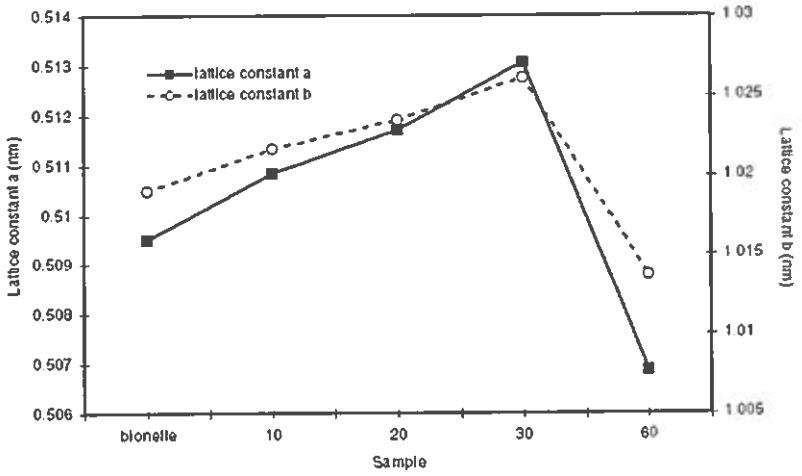
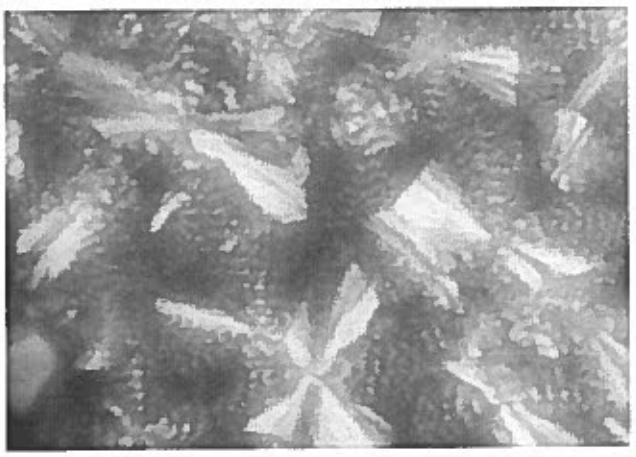


Figure 7 Polarizing optical micrographs of PBS spherulites obtained at 90°C



intensity profiles of PBS fibers at various take-up speeds. For comparison, as mentioned before, Ihn et al[2] found that the lattice parameters of the PBS crystal in the monoclinic unit cell in a single crystal were a = 0.523 nm and b = 0.908 nm.

Considering lattice constants from WAXD meridian scan intensity profiles of PBS fibers, samples obtained at 10 and 20 m/min take-up speed showed a lower lattice constant "a" than 0.523 nm. In all cases, samples showed a higher lattice constant "b". In WAXD equatorial intensity profiles, the lattice constant "a" was always lower than predicted, and the lattice constant "b" was higher. In all the PBS fiber samples, the results were near to those predicted for "a" and "b" lattice constants. All of these changes in lattice constants are produced by molecular orientation during extrusion.

Finally, we obtained spherulites from PBS. In **Figure 7** is possible to observe from polarizing optical micrographs that crystals are formed like a Maltese cross at 90 °C as mentioned in the literature[2]. They showed extinction rings, too.

CONCLUSIONS

Fibers from PBS were obtained using a single screw extruder at various take-up speeds. These changes improved some of the properties of PBS fibers because of changes in molecular orientation and crystallinity.

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