생분해성 폴리부틸렌숙시네이트 필름의 구조 및 성질에 미치는 초기 고분자 농도의 영향

류원석, 최진현[*], 지병철[*], 유영태[**],
영남대학교 섬유패션학부, [*]경북대학교 염색공학과, [**]건국대학교 공업화학과

Effect of Initial Polymer Concentration on the Structure and Properties of Biodegradable Poly(butylene succinate) Film

Won Seok Lyoo, Jin Hyun Choi[*], Byung Chul Ji[*], and Youngtai Yoo[**]
School of Textiles, Yeungnam University, Kyongsan, Korea
[*]Department of Dyeing and Finishing, Kyungpook National University, Taegu, Korea
[**]Department of Industrial Chemistry, Kon Kuk University, Seoul, Korea

1. Introduction

Poly(butylene succinate) (PBS) is one of the most promising materials for biodegradable application as fibers, nonwovens, films, sheets, and bottles [1]. To prepare the best PBS film for particular use, the type and amount of crystal, degree of crystallinity and orientation, and mechanical properties should be controlled. For an effective control of these factors, general hot drawing of biodegradable film and fiber prepared through melt casting and melt spinning have been in progress actively [2-4]. However, such attempts have two problems: Firstly, melt-processed specimens which are disadvantageous in revealing higher orientations were used. Secondly, a hot drawing method with higher probabilities of microcrystallite formation, back folding of molecular chains, and thermal degradation of samples was adopted.

Drawability and orientation of polymer depends on the initial concentration of polymer solution from which the film is made. Proper level of entanglements is needed to increase the orientation of polymer chain and it can be realized by the control of solution concentration.

Zone drawing technique [5-8], a method inducing a necking on one point of a film by heat, can minimize the disadvantages of hot drawing.

In this study, the effects of initial polymer concentration on the structure, physical properties, and biodegradability of PBS film were investigated. A convenient one-step zone drawing method was introduced for fine control of physical properties and for higher orientation of solution-cast PBS film.

2. Experimental

2.1 Polycondensation

The monomer mixture of succinic acid and 1,4-butanediol were melt and stirred at 190 ℃ for 2 h in a reactor. Then, titanium tetrabutoxide (0.3 wt% of monomer) was charged to the reactor and the reaction temperature was raised to 240 ℃ over a period of 30 min. The reactant was maintained for 2-7 h depending on the feed composition. The number-average molecular weight of PBS determined by the viscosity method was 37,000.

2.2 Preparation of PBS film

The concentrations of PBS/chloroform solutions used in film casting were 8, 11, 14, 17, and 20 g/dl, respectively. The homogenized solution was poured into a stainless steel dish and dried under vacuum at 25 ℃ for about 10 days. After chloroform was removed from the films, the dried films having similar thickness of about 155 μm were obtained.

2.3 Zone drawing of PBS film

Zone drawing of PBS film (1 cm width and 10 cm length) was carried out at several temperatures under tensions controlled by different dead weights, respectively.

2.4 Characterization of PBS film

The measurement of birefringence and the observation of film surface were carried out on a polarizing optical microscope.

Wide angle X-ray diffractograms were obtained to measure the degree of crystallinity of the film. Wide angle X-ray diffraction (WAXD) patterns were obatined using Statton camera.

The tensile strength and modulus of PBS film were obtained from load-elongation curve.

For the test of the microbial and hydrolytic degradation, PBS film, incubated in phosphate buffer solution (pH 7.0) with lipase from *Rhizopus arrihzus* at 37 ± 1 ℃, was weighed after drying. The solution was filtered and total organic carbon (TOC) formation was measured.

3. Results and Discussion

In this study, firstly, relative viscosity measuring experiments were tried to predict optimum polymer concentration of PBS. A critical polymer concentration of 14 g/dl showing an abrupt change in the solution viscosity was obtained. To confirm this result, we tried to determine optimum polymer concentration of PBS solution by zone drawing method.

The maximum value of draw ratio appeared at solution concentration of 14 g/dl, irrespective of drawing stress, drawing temperature, and heat band speed. At lower or higher concentration, draw ratio decreased gradually. This attributes to a suitable number of entanglements, that can be evaluated by determination of optimum solution concentration. Also, the maximum birefringence appeared at solution concentration of 14 g/dl. In contrast, the crystallinities of the zone-drawn PBS films having same draw ratios were nearly constant, despite of different initial polymer concentrations.

WAXD photographs of three PBS films having similar draw ratios of 4 prepared from different initial concentrations are shown Figure 1. It showed that the highest orientation appeared at solution concentration of 14 g/dl in spite of similar draw ratios about 4 and similar degrees of crystallinity of 62-63%. This indicates that the film prepared at solution concentration of 14 g/dl, which has a suitable number of entanglements, is more oriented than those at other concentrations.

Figure 2 shows the surface morphologies of the PBS films having similar draw ratios of about 4, similar film thicknesses of 45 μm, and similar degrees of crystallinity of 62-63% cast at different initial solution concentrations. Microfibrillar morphology containing highly oriented PBS chains is illustrated in Figure 2b. That is, it was possible to effectively draw PBS film prepared at initial concentration of 14 g/dl. In contrast, in the case of higher concentrations, some lamellar structures due to poor chain orientation arising from higher chain entanglements in film was observed (Figure 2d).

In addition, the tensile properties of PBS film having similar draw ratio and similar crystallinity were highest at 14 g/dl. The hydrolytic degradation rate of the film at 14 g/dl was lowest, indicating that the degradation behaviors were greatly affected by the initial polymer concentration, orientation, and crystal morphology.

4. References

1) R. W. Lenz, *Adv. Polym. Sci.*, **107**, 1(1993)
2) M. Mochizuki, M. Hirano, Y. Kanmuri, K. Kudo, and Y. Tokiwa, *J. Appl. Polym. Sci.*, **55**, 289(1995).
3) S. H. Lee, K. H. Lee, and S. K. Hong, *J. Appl. Polym. Sci.*, **64**, 1999(1997).
4) M. Mochizuki, K. Mukai, K. Yamada, N. Ichise, S. Murase, and Y. Iwaya, *Macromolecules*, **30**, 7403(1997).
5) T. Kunugi and Y. Akiyama, *Polymer*, **23**, 1199(1982).
6) T. Kunugi, T. Kawasumi, and T. Ito, *J. Appl. Polym. Sci.*, **40**, 2101(1990).
7) S. S. Han, W. S. Yoon, J. H. Choi, S. Y. Kim, B. C. Ji, and W. S. Lyoo, *J. Appl. Polym. Sci.*, **66**, 1583(1997).
8) W. S. Lyoo, S. S. Han, J. H. Choi, Y. W. Cho, and W. S. Ha, *J. Korean Fib. Soc.*, **32**, 1023(1995).

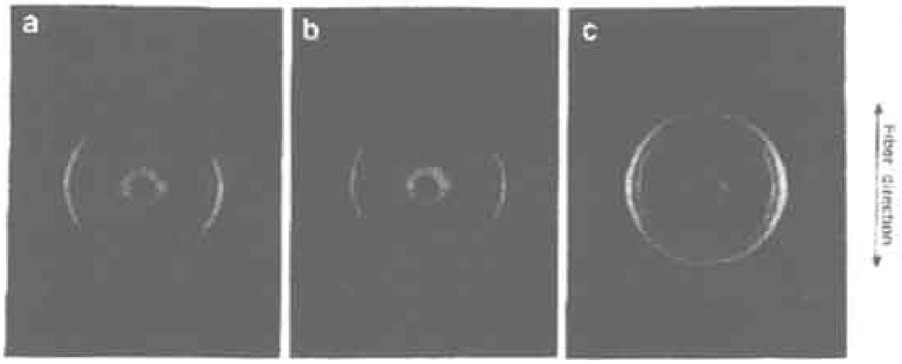

Figure 1. WAXD photographs of the one-step zone-drawn PBS film having similar draw ratios prepared at three different initial concentrations: a, 11 g/dl, draw ratio of 4.0; b, 14 g/dl, draw ratio of 3.9; c, 17 g/dl, draw ratio of 3.9.

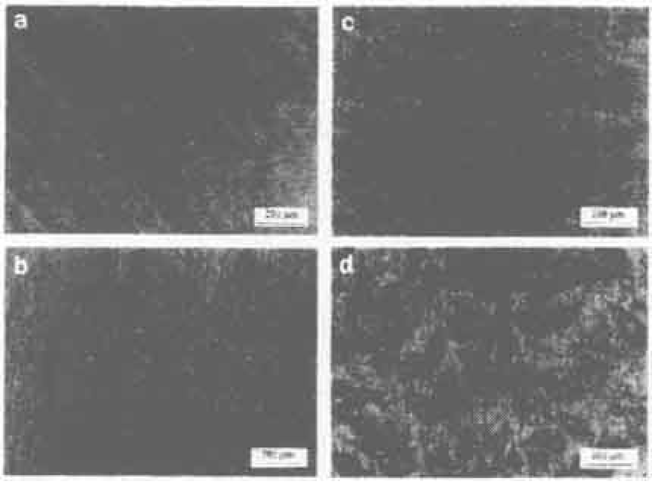

Figure 2. Polarizing micrographs of the surfaces of the one step zone-drawn PBS film having similar draw ratios prepared at four different initial concentrations: a, 11 g/dl, draw ratio of 4.0; b, 14 g/dl, draw ratio of 3.9; c, 17 g/dl, draw ratio of 3.9; d, 20 g/dl, draw ratio of 4.0.