

Effects of polymer concentration and zone drawing on the structure and properties of biodegradable poly(butylene succinate) film

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Abstract

To produce various biodegradable poly(butylene succinate) (PBS) films for particular use, the effects of initial polymer concentration and zone drawing on the structure, physical properties, and hydrolytic degradation of PBS film were investigated. PBS films were prepared from chloroform solutions with different initial concentrations of 8, 11, 14, 17 and 20 g/dl. In order to investigate the drawing behavior of the PBS films with different solution concentrations, the films were drawn under various zone drawing conditions. Through a series of experiments, it turned out that the initial concentration of PBS solution in chloroform caused significant changes in the draw ratio of the PBS film. That is, the zone draw ratios of the film at initial concentration of 14 g/dl exhibited its maximum values and gradually decreased at higher or lower concentrations. Thus, it was concluded that the initial concentration of 14 g/dl is the optimum polymer concentration to produce maximum draw ratio in this work. In addition, the crystal and amorphous orientations and tensile properties of PBS film having similar draw ratio and similar crystallinity were highest at 14 g/dl and surface crystal morphologies of these films were absolutely different. The hydrolytic degradation rate of the film at 14 g/dl was lowest, but with similar draw ratio, film dimension, and crystallinity, indicating that the degradation behaviors were greatly affected by the initial polymer concentration, orientation, and crystal morphology. © 2000 Published by Elsevier Science Ltd.

Keywords: Poly(butylene succinate) film; Initial polymer concentration; Maximum draw ratio

1. Introduction

Aliphatic polyesters like poly(butylene succinate) (PBS) are one of the most promising materials for biodegradable fibers, nonwovens, films, sheets, and bottles [1]. Among them, films used for packaging materials and agricultural films have received much attention due to their great potential for market [2–6]. To prepare the best film for particular use, many parameters related to the structure and properties of film should be considered. One of the most important factors affecting the biodegradability of film is the structure and physical properties such as the type and amount of crystal, degree of crystallinity and orientation, and mechanical properties [7–12]. Thus to control these factors, general hot drawings of biodegradable film and fiber, which are prepared through melt casting and melting spinning have been in progress actively [13–15]. However, these attempts

described above have two problems in producing various films having high and regular chain orientations and good physical properties accompanied by fine and easy control of properties for a particular use. Firstly, melt-processed specimens, which are disadvantageous in revealing higher orientations were used. Secondly, a hot drawing method with higher probabilities of microcrystallites formation, back folding of molecular chains, and thermal degradation of sample was adopted [16–21].

As is well known, molecular weight [20,22–25], molecular weight distribution [26], and concentration of polymer solution [27,28] have a marked influence on the drawability (orientation) of polymers. Generally, the drawability increases as the molecular weight increases [29]. Under the same molecular weight, this property depends principally on the initial concentration of the polymer solution from which the film was made [22,27]. This is due to a reduced number of entanglements per molecule in the solution cast or spun polymers in comparison with those obtained from the melt [30]. That is, the macromolecules

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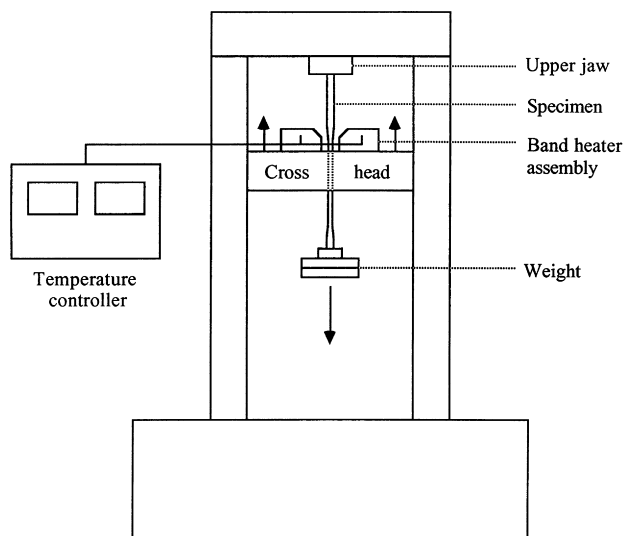


Fig. 1. Schematic representation of zone drawing apparatus.

are thought to form transient network with entanglements acting as friction centers or nonlocalized junctions. Because high entanglement density impedes large deformation of solidified high molecular weight polymers, their drawability might be improved by reduction of the number of entanglements. However, in the case of dilute solution, which has fewer entanglement, maximum draw ratio cannot be obtained owing to rare coil overlap and chain slippage occurred at drawing step. Therefore, 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 [17,20,21,25], a method inducing a necking on one point of a film by heat, has many advantages described above compared with hot drawing method. It reveals that the higher orientation is significantly related to zone draw ratio [16,18,19].

In this study, the effects of initial polymer concentration and zone drawing on the structure and physical properties like crystal morphology, crystallinity, orientation, and mechanical properties and biodegradability of PBS film [2,3,6], which is one of the most important biodegradable polymers for having acceptable mechanical properties and comparable softening temperature to low-density polyethylene and polystyrene were investigated. A convenient one-

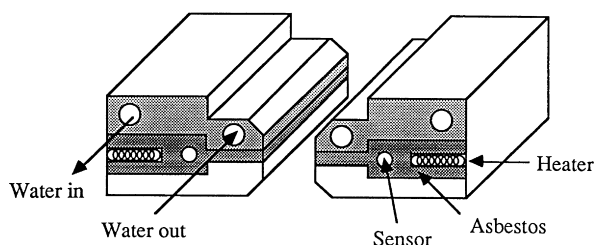


Fig. 2. Schematic representation of band heater assembly.

Table 1
Zone drawing conditions of PBS film

Drawing stress (MPa)	0.25, 0.50, 0.75, 1.00, 1.50, 3.00, 4.50, 6.00
Drawing temperature (°C)	70, 90, 110
Heat band speed (mm/min)	1, 5, 10, 20

step zone drawing method was introduced for fine controlling physical properties and for obtaining higher orientation of solution-cast PBS film.

2. Experimental

2.1. Material and polymerization

Succinic acid and 1,4-butanediol (Junsei Chem.) were used without further purification. Titanium tetrabutoxide (TTB) was obtained from Aldrich and used as-received. PBS was prepared employing two-step polymerization route [31]. Firstly, calculated amounts of succinic acid and diols (1:1.2 by mole ratio) were introduced to a reactor equipped with an overhead stirrer and a temperature control device. The monomer mixture was melted and stirred at 190°C for 2 h. Evolved water was removed passing through a condensation column. Then, TTB catalyst (0.3 wt% of monomer) was charged to the reactor and the reaction temperature was raised to 240°C over a period of 30 min gradually applying a reduced pressure to remove low molecular weight condensates and maintained for 2–7 h depending on the feed composition. The number-average molecular weight (M_n) of PBS was determined by the viscosity method. Chloroform was used as a solvent. The intrinsic viscosity $[\eta]$ at 25°C was obtained by using Ubbelohde viscometer. From Eq. (1), M_n was calculated to be 37,000 in this study:

$$[\eta] = 2.15 \times 10^{-4} [M_n]^{0.82}. \quad (1)$$

2.2. Preparation of PBS film

Relative viscosity of PBS solution was measured at 25°C by using Ubbelohde capillary viscometer. From these results, reduced viscosity for film casting was calculated. The concentrations of PBS solution in chloroform 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°C for about 10 days. After chloroform was removed from the films, the dried films having similar thickness of 155 μm were obtained.

2.3. Zone drawing of PBS film

Zone drawing was carried out at several temperatures by moving a pair of narrow band heaters with dimensions in

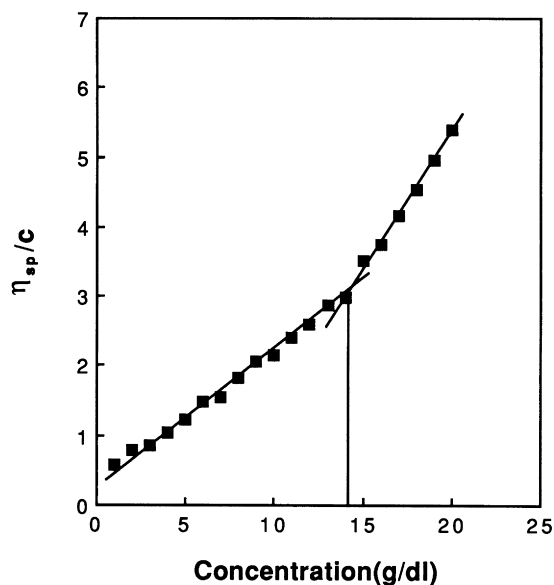


Fig. 3. Reduced viscosity of PBS solution in chloroform at 25°C with solution concentration.

length of 7 cm, in width of 2.5 cm, and in thickness of 1 mm along the film (Fig. 1). The film of 155 μm thickness, 1 cm width and 10 cm length was drawn under tensions controlled by different dead weights, respectively, on an Instron model 4201 (Fig. 2) [21,25,32,33]. The zone drawing conditions are listed in Table 1.

2.4. Characterization of PBS film

Birefringences were measured on a polarizing microscope with senarmont compensator (Nikon, Optiphot-Pol 104). The birefringence was determined by dividing the optical path length by the thickness. Film surface was observed by polarized optical microscope (POM) (Nikon, Optiphot-Pol 104).

Wide angle X-ray diffractograms of PBS film for determinations of crystallinity were obtained with a nickel-filtered $\text{CuK}\alpha$ radiation (40 kV, 200 mA) using X-ray diffractometer (Mac Science, MXP-18). To measure the degree of crystallinity of the film, the X-ray diffraction patterns were recorded in the range of $2\theta = 5\text{--}65^\circ$ at a scan speed of $1^\circ/\text{min}$. X-ray crystallinity was calculated by using a basic method for differentiation between crystalline and amorphous scattering in diffraction intensity curves [34]. Wide-angle X-ray diffraction (WAXD) patterns were obtained by Statton camera with flat-plate geometry using Ni-filtered $\text{CuK}\alpha$ radiation at 40 kV and 45 mA. X-ray pattern of the PBS was recorded on Kodak direct exposure film using pinhole collimation under vacuum. The exposure times for WAXD was 12 h.

Load–elongation curves were recorded on an Instron model 4201 using a sample length of 2 cm and a cross-head speed of 100 mm/min. The tensile strength and

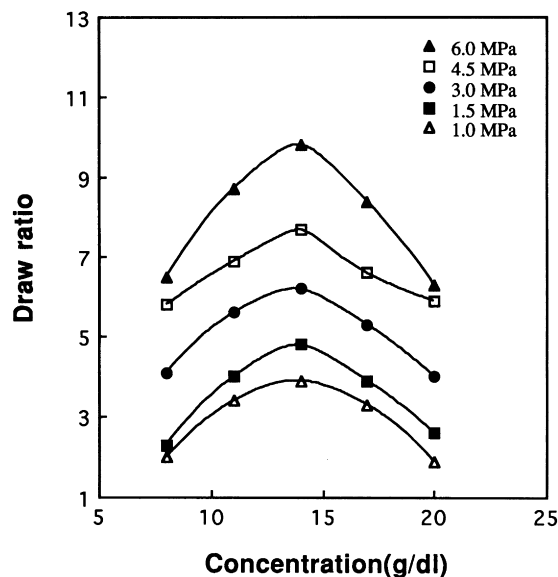


Fig. 4. Zone draw ratio of PBS film drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with concentration of PBS solution.

modulus of the PBS film were the average values of 20 samples, respectively.

Microbial and hydrolytic degradations of PBS film having similar thickness of about 45 μm and similar draw ratio of about 4 were studied as follows: the film specimens was immersed in a vial containing 50 mM phosphate buffer solution (pH 7.0) with 5 units/ml of lipase from *Rhizopus arrhizus* (Sigma chemical). The vial was then placed in a temperature controlled incubator ($37 \pm 1^\circ\text{C}$) at a shaking speed of 70 rpm for a fixed time. After incubation, each film was periodically taken from the solution and was carefully weighed after drying under reduced pressure. The solution was filtered through a 0.25 mm filter and water-soluble total organic carbon (TOC) formation was measured with Shimadzu TOC-5000.

3. Results and discussion

3.1. Determination of optimum concentration using viscosity and drawability

In general, it has been known that the draw ratio of solution-cast film is influenced by the solution concentration and maximum draw ratio can be obtained at a certain solution concentration. Moreover, in the vicinity of this concentration the solution viscosity steeply increases. Thus, in this study, firstly, relative viscosity measuring experiments were tried to predict optimum polymer concentration of PBS, as shown in Fig. 3. From the fact that all the measured data were approximated to two different linear lines in Fig. 3, it can be identified that a critical polymer concentration of 14 g/dl showing an abrupt change in the solution viscosity

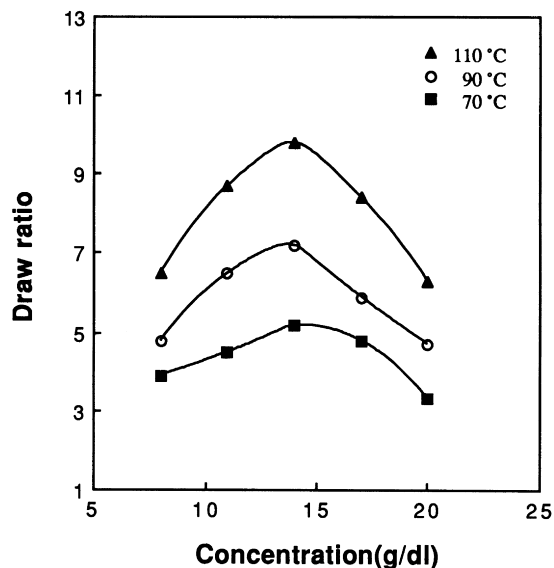


Fig. 5. Zone draw ratio of PBS film drawn under various drawing temperatures, drawing stress of 6 MPa, and heat band speed of 1 mm/min with concentration of PBS solution.

is present. To confirm viscometry data, we tried to determine optimum polymer concentration of PBS solution by zone drawing method. The structure and physical properties of zone-drawn film may vary with the conditions of preparation and drawing of film. That is, firstly, initial concentration of polymer solution during preparation of the film, also, secondly, processing parameter like drawing stress, drawing temperature, and heat band speed during drawing of film have marked influences on the drawing behavior of film. In this study, effects of those factors on the draw ratios of films were investigated.

Fig. 4 shows the zone draw ratios of PBS films drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min as a function of initial solution concentrations. The draw ratio increased with an increase in the drawing stress. Also, maximum value up to 9.8 could be obtained at drawing stress of 6 MPa. This result can be explained that deformation of molecular chains increases with increasing drawing stress above glass transition temperature. Under higher drawing stress of over 6 MPa, a breakage of film occurs. The maximum value of draw ratio appeared at solution concentration of 14 g/dl. At lower or higher concentration, draw ratio decreased gradually. This attributes to a suitable number of entanglements for the film prepared at solution concentration of 14 g/dl. Generally, for effective drawing, film must have a suitable number of entanglements, that can be evaluated by determination of optimum solution concentration. Optimum initial concentrations of polymer solutions vary with molecular weight, linearity, and stereoregularity of polymers and type of solvent, etc. In this study, however, those effects were negligible because same types of polymer with same molecular weight and same solvent were used in all the experiments. Therefore, it can be supposed that initial

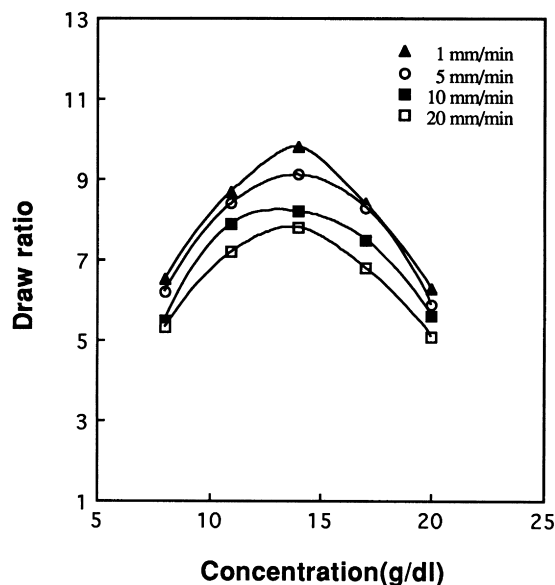


Fig. 6. Zone draw ratio of PBS film drawn under various heat band speeds, drawing stress of 6 MPa, and drawing temperature of 110°C with concentration of PBS solution.

concentration of 14 g/dl is the optimum concentration, which contains suitable entanglements. The general viscometric method for the determination of optimum solution concentration is complicated and requires long time and so zone drawing method could be the better choice for its determination.

Fig. 5 shows the zone draw ratios of PBS films drawn under various drawing temperatures, drawing stress of 6 MPa, and heat band speed of 1 mm/min as a function of the initial solution concentrations. Draw ratio increased for each film with increasing drawing temperature. This implies that as drawing temperature reaches melting temperature (115°C) of undrawn PBS film, degree of freedom of PBS chains increases. The largest value was obtained at concentration of 14 g/dl, so this can be presumed to be the optimum concentration manifesting the highest draw ratio.

Fig. 6 shows the zone draw ratios of PBS films drawn under various heat band speeds, drawing stress of 6 MPa, and drawing temperature of 110°C as a function of the initial solution concentrations. It was shown that the slower is the heat band speed, the larger is the draw ratio. This may lead to the conclusion that a softening of film becomes easier owing to longer residence time for film between two heat bands. That is, more uniform heat transfer to the sample of slower heat band speed had a great effect on the draw ratio of PBS film. As identified in Figs. 4–6, zone draw ratio of film prepared at concentration of 14 g/dl was the largest among all the films of different concentrations. Thus, it was supposed that the film prepared at this concentration has suitable entanglements to attain effective draw ratio. Conclusively, it can be predicted that the present method determining optimum initial concentration of PBS solution by zone draw ratio is correct and suitable.

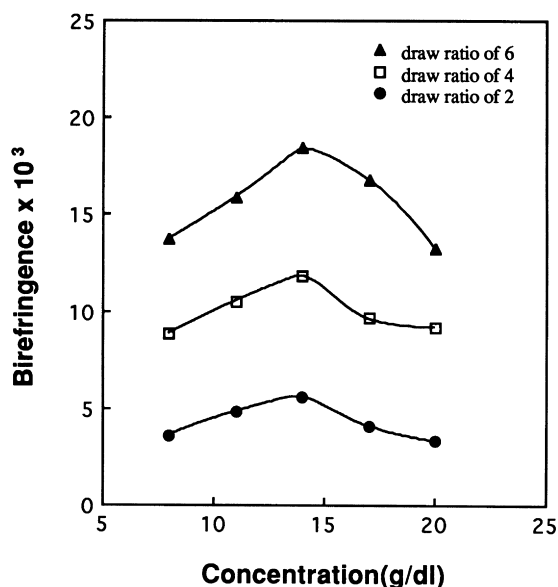


Fig. 7. Birefringence of PBS film zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with draw ratio.

3.2. Effect of initial concentration and draw ratio on the structure and properties of the film

The effect of initial polymer concentration on the birefringence of the PBS film zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with draw ratios are shown in Fig. 7. Nevertheless, in specimens having similar draw ratios of about 2, 4, and 6, respectively, concentration effect is obvious. It was shown that the maximum birefringence appeared at solution concentration of 14 g/dl. At lower or

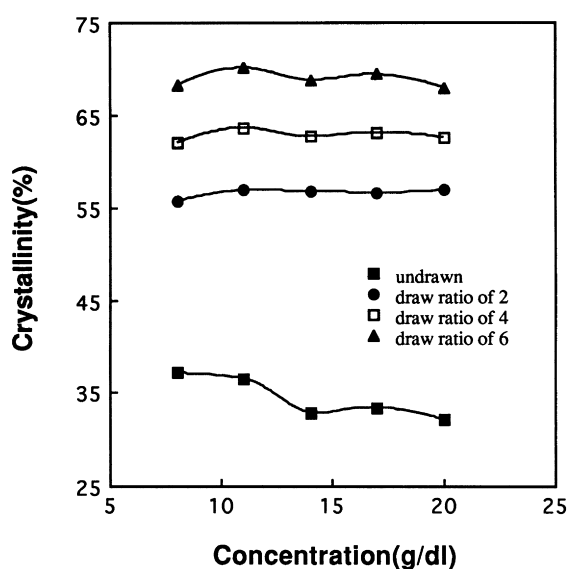


Fig. 8. Crystallinity of PBS film zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with draw ratio.

higher concentrations, birefringence decreased. This demonstrates that the degree of overall orientation of the PBS film cast at 14 g/dl, the concentration of maximum drawability, is the highest than those cast at the other concentrations. Moreover, birefringence of film increased with an increase in the draw ratio. It was thought that much more heat transfer to the sample of longer drawing time had a great effect on the birefringence of the film.

Fig. 8 presents the crystallinities of PBS films zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with draw ratios. As draw ratio increased, crystallinity increased at all polymer concentrations. This result well agreed to the previous draw ratio and birefringence data. However, it is interesting to see that the crystallinities of the zone-drawn PBS films having same draw ratios were nearly constant, but with different initial polymer concentrations.

WAXD photographs of three PBS films having similar draw ratios of 4 prepared from different initial concentrations are shown in Fig. 9. It showed that the highest orientation appeared at solution concentration of 14 g/dl but with similar draw ratios of about 4 and similar degrees of crystallinity of 62–63%. At lower or higher concentration, orientation of the film decreased. 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. This result is well coincident with that in Fig. 7.

Fig. 10 shows the surface crystal 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 was shown in Fig. 10b. 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. From the fact that the drawn PBS films had structural differences in the surface crystal morphologies according to the initial solution concentrations, but with similar draw ratios and degrees of crystallinity, it could be supposed that the initial polymer concentration of the PBS film had a marked influence on the deformability and crystal shape of PBS film.

The effect of initial polymer concentration on the tensile strength (a) and the tensile modulus (b) of the PBS films zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min is shown in Fig. 11. It is clear that the tensile strength and tensile modulus of the PBS film increased significantly with draw ratio. It is also noted from Fig. 11 that tensile strength and tensile modulus of the PBS film showed maximum value at 14 g/dl concentration. The maximum tensile strength and tensile modulus obtained in maximum drawn PBS film cast at 14 g/dl

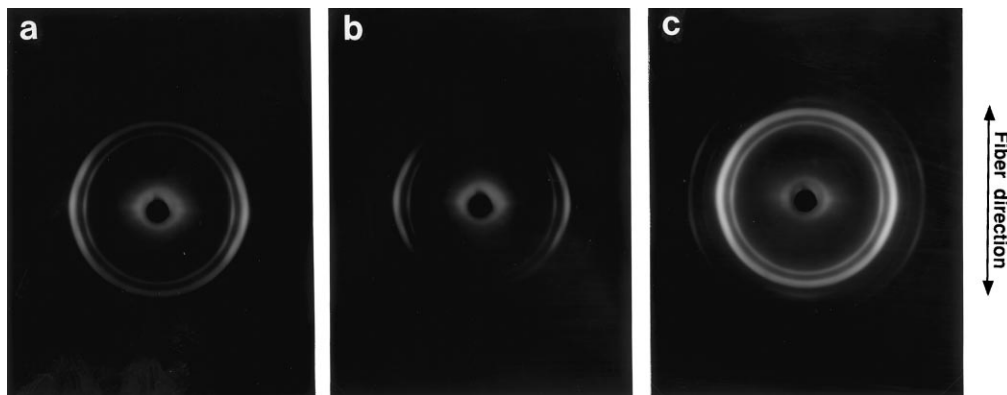


Fig. 9. WAXD photographs of the one-step zone-drawn PBS film having similar draw ratios prepared at three different initial concentrations: (a) 11 g/dl, draw ratio of 4.0; (b) 14 g/dl, draw ratio of 3.9; and (c) 17 g/dl, draw ratio of 3.9.

were 0.71 and 9.4 GPa, respectively. Salmawy et al. [35] reported that the draw ratio, tensile strength, and tensile modulus of PBS fiber prepared by melt spinning were 4–12, 0.3–0.9 and 0.9–2.2 GPa, respectively. Two specimens had similar molecular weights (M_n) of 37,000 (ours) and 44,000 (Salmawy et al.). From the fact that two PBS specimens had remarkable differences in the tensile modulus, but with similar molecular weight and

draw ratio, it might be supposed that the initial polymer concentration (melt or solution) had an important influence in preparing PBS fibrous materials. It was observed that the film having optimum macromolecular entanglements cast from 14 g/dl solution, represented higher drawability, degree of orientation, tensile strength and tensile modulus than other films. In general, the fact that the film represents high tensile

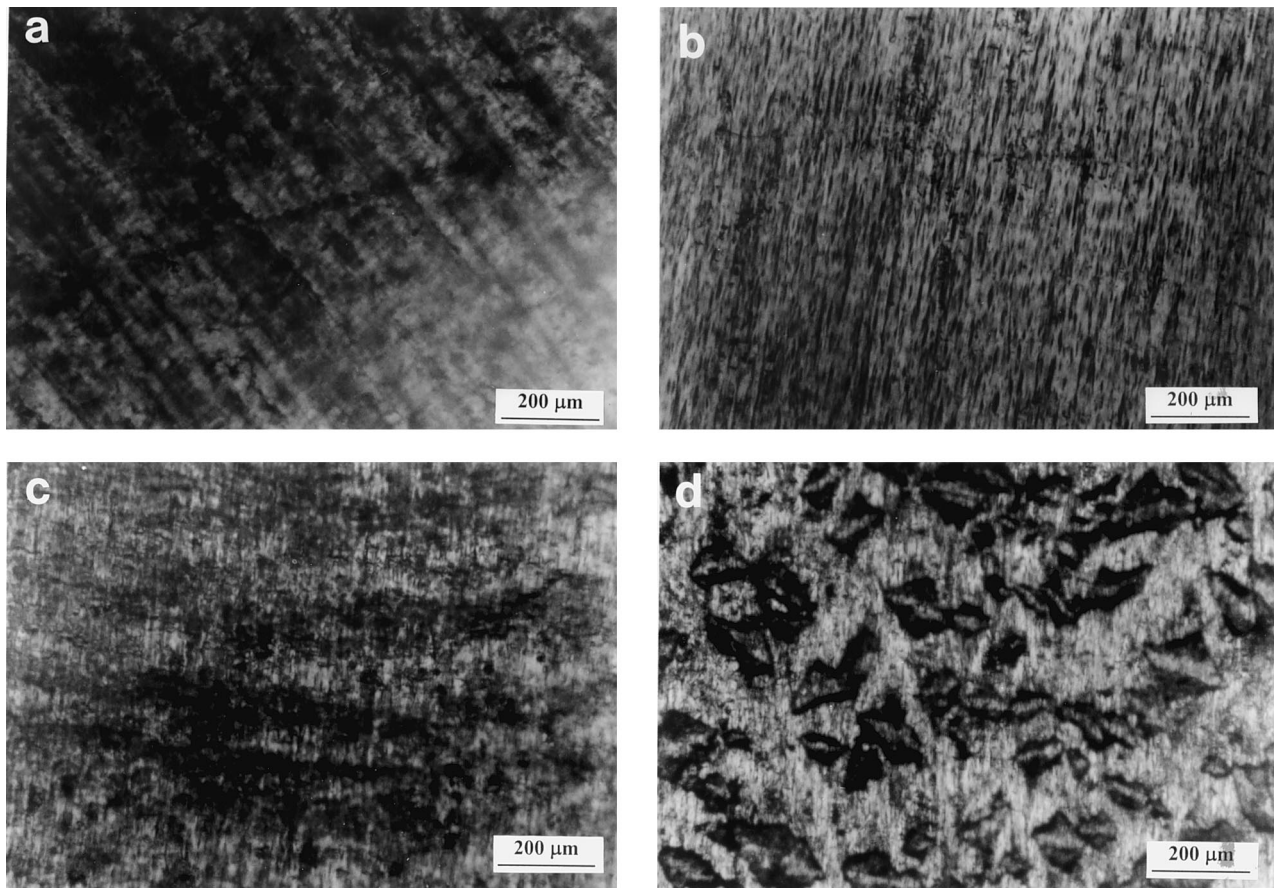
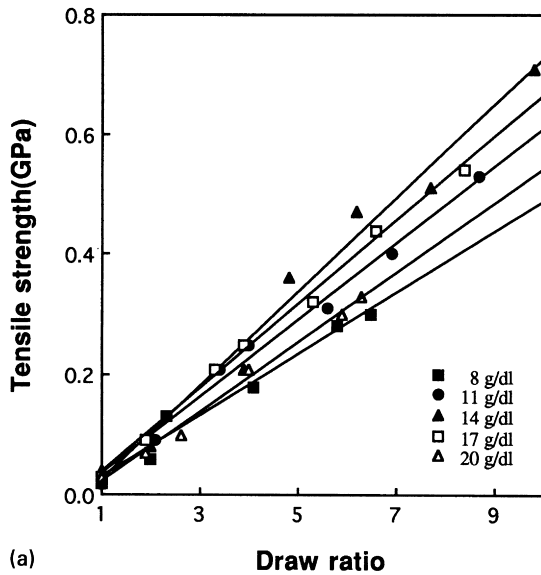
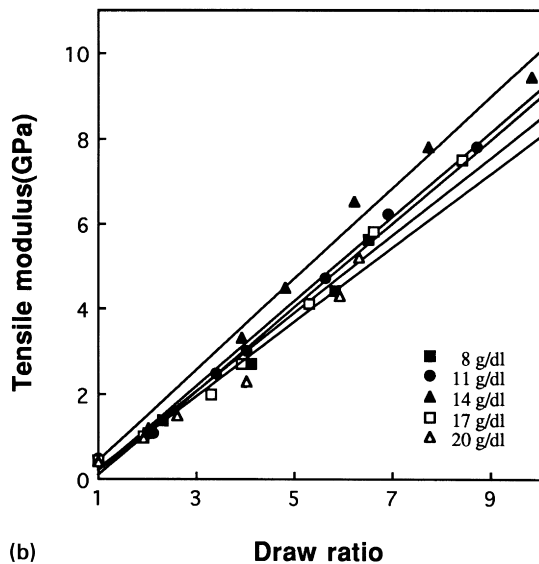


Fig. 10. Polarizing micrographs of the surfaces of the one-step zone-drawn PBS film having similar draw ratios prepared at four different initial concentrations: (a) 11 g/dl, draw ratio of 4.0; (b) 14 g/dl, draw ratio of 3.9; (c) 17 g/dl, draw ratio of 3.9; and (d) 20 g/dl, draw ratio of 4.0.



(a)



(b)

Fig. 11. Tensile strength (a) and tensile modulus (b) of PBS film zone-drawn under various drawing stresses, drawing temperature of 110°C, and heat band speed of 1 mm/min with draw ratio.

strength and tensile modulus means that the polymer has the suitable length of tie molecules and uniform length distribution. The PBS film cast at 14 g/dl represented higher tensile strength and tensile modulus than the PBS films cast at other concentrations because the film had suitable tie molecule and uniform length distribution. The PBS films cast at higher concentrations had too many tie molecules, which prevented the orientation of chains, so, tensile strength and tensile modulus were lowered. The PBS films cast at lower concentrations had fewer tie molecules, so, tensile strength and tensile modulus were lowered due to slippage of molecular chains.

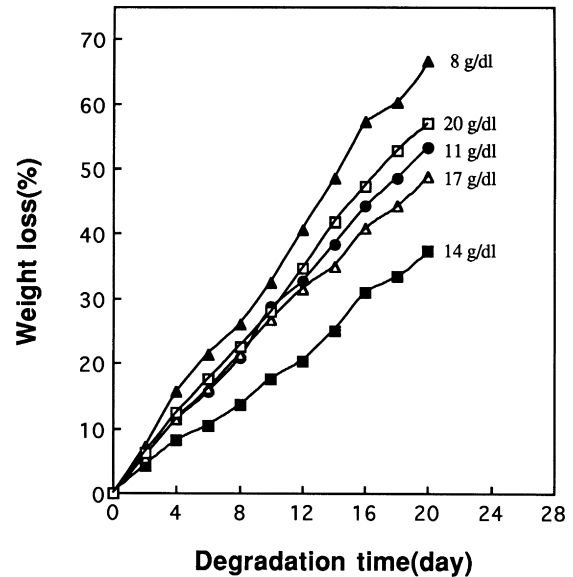


Fig. 12. Degradation profile of the one-step zone-drawn PBS film having similar draw ratios of about 4 and thicknesses of 45 μm prepared at five different initial concentrations.

3.3. Effect of initial concentration on the biodegradability

In this study, to clarify the effects of the initial polymer concentration, orientation, and crystal morphology on the microbial and hydrolytic degradations of the PBS film, we used the PBS films with same draw ratios of 4, same film thicknesses of 45 μm , and same degrees of crystallinities of 62–63% in the biodegradability test. Fig. 12 shows the results. In the degradations of the PBS films as plotted in Fig. 12 for a period of 20 days the degradation rate was greatly affected by the initial polymer concentration. That is, the degradation rate of the PBS films at 14 g/dl having highest orientations and largest crystallite size, which was calculated from the WAXD pattern, was lowest, but with nearly same crystallinities of all films used. From these results, it is concluded that chain orientation and crystallite size obtained by fine controls of initial polymer concentration and zone-draw ratio have a marked influence on the biodegradability of the PBS film.

4. Conclusions

The optimum processing condition for the biodegradable PBS film was investigated by measuring the birefringence, degree of orientation, crystallinity, tensile properties, and biodegradability in terms of the initial polymer concentration and draw ratio. PBS films were prepared from chloroform solutions with different initial concentrations of 8, 11, 14, 17, and 20 g/dl. In order to investigate the drawing behavior of the PBS films with different solution concentrations, the films were drawn under various zone drawing conditions. From several results, it was identified

that the initial concentration of PBS solution in chloroform caused significant changes in the draw ratio of the PBS film. That is, the zone draw ratios and tensile properties of the film at initial concentration of 14 g/dl exhibited its maximum values and gradually decreased at higher or lower concentrations. In case of maximum drawn PBS film, the draw ratio of 9.8, tensile strength of 0.71 GPa, and tensile modulus of 9.4 GPa were obtained, respectively. Such high properties were well correlated with the maximized birefringence and crystal and amorphous orientations and tensile properties of the PBS film at 14 g/dl were the highest among the films cast at five different initial polymer concentrations, but with same draw ratio and same crystallinity. It was identified that these physical properties described above had a marked influence on the biodegradability of the PBS film. Conclusively, it is possible to produce various PBS films having different physical properties and biodegradabilities at different initial polymer concentrations by adopting simple zone drawing method. In the near future, we will report on the comparison of the biodegradation behaviors of the PBS films having various structures and physical properties prepared by our zone drawing and general hot drawing methods, respectively.

Acknowledgements

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