

Role of Initial Polymer Concentration in the Physical Properties of Zone-Drawn Biodegradable Poly(butylene adipate) Film

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ABSTRACT: The effects of initial polymer concentration and zone drawing on the physical properties and hydrolytic degradation of poly(butylene adipate) (PBA) film were investigated to prepare PBA film with various biodegradabilities and physical properties for particular uses. It was identified from the results that the initial concentration of PBA solution in chloroform caused significant changes in draw ratio of the PBA film. The maximum draw ratio of 8.2, tensile strength of 0.59 GPa, and tensile modulus of 7.8 GPa were obtained at the initial concentration of 12 g/dL, measured as an optimum polymer concentration for film casting. The chain orientations and tensile properties of the PBA film cast at this concentration were superior to those of the PBA films cast at the other concentration, although they had the same draw ratio and similar crystallinity. The hydrolytic degradation rate of the film cast at 12 g/dL was lowest among the films having the same draw ratio, film dimension, and crystallinity, indicating that degradation behaviors were greatly affected by the initial polymer concentration and the molecular orientation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1–7, 2001

Key words: zone drawing; PBA; biodegradability; maximum draw ratio; optimum polymer concentration

INTRODUCTION

Poly(butylene adipate) (PBA), an aliphatic polyester, is one of the most promising materials with excellent biodegradability as a form of fiber, non-

woven, film, sheet, or bottle.¹ Among them, biodegradable films for packaging and agricultural utilities have received much attention due to their great potential for market.^{2–6} In this sense, many parameters related to the structure and properties of a film should be considered. Several important factors affecting the biodegradability of a film are crystal types, degree of crystallinity and orientation, and mechanical properties.^{7–12} Thus, to control these factors, general hot drawing of melt-cast film or

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melt-spun fiber with biodegradability has been in progress actively.^{13–15} However, the melt-processed specimens are disadvantageous in revealing a high degree of orientation, and the hot drawing method has a higher probability of microcrystallite formation, a back folding of molecular chains, and a thermal degradation of a sample.^{16–21} The zone drawing technique,^{17,20–22} a method inducing a necking on one point of a film by heat, has many advantages in overcoming the drawbacks of the hot drawing. Moreover, in previous reports^{16,18,19} it was known that the higher orientation was obtained by zone drawing.

In the case of a solution-cast film or a solution-spun fiber, polymer concentration^{23,24} has a marked influence on drawability and orientation of polymers due to a reduced number of entanglements per molecule compared with melt-processed film or fiber.²⁵ Because high entanglement density impedes large deformation of solidified polymers, their drawability might be improved by reduction of the number of entanglements. On the contrary, in the case of a dilute solution, where polymers possess fewer entanglements, the maximum draw ratio cannot be obtained because of insufficient coil overlap and chain slippage. Therefore, the level of entanglements should be optimized by controlling solution concentration to enhance the orientation and mechanical properties of polymer.

For the practical utility of a biodegradable polymer, the physical properties should be controlled as a state that biodegradable nature be maintained. In this study, the zone drawing method was introduced for fine control of physical properties and higher orientation of a solution-cast PBA film, which is one of the most important biodegradable polymers for having acceptable mechanical properties and softening temperature comparable to low-density polyethylene. That is, the effects of initial concentration of polymer solution on the crystallinity, orientation, mechanical properties, and biodegradability of the zone-drawn PBA film were investigated.

EXPERIMENTAL

Materials

Adipic acid and 1,4-butanediol (Junsei Chem.) were used without further purification. Titanium tetrabutoxide (TTB) was obtained from Aldrich and used as received. PBA was prepared employing a two-step polymerization route.²⁶ At first, the

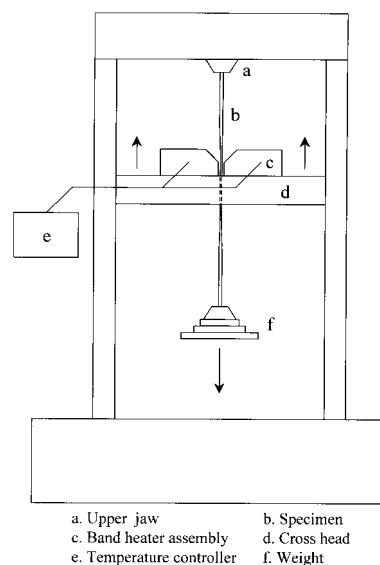


Figure 1 Schematic representation of the zone drawing apparatus.

monomer mixture of adipic acid and diols (1 : 1.2 by mol ratio) was melt and stirred at 190°C for 2 h. Then, TTB catalyst (0.3 wt % of the monomer mixture) was charged to the reactor. Reaction temperature was raised up to 240°C over a period of 30 min gradually with applying a reduced pressure to remove low molecular weight condensates, and was maintained for 2–7 h, depending on the feed composition. The number-average molecular weight of PBA determined from intrinsic viscosity in chloroform was 45,000.

Measurement of Relative Viscosity

Relative viscosity of the PBA solution was measured at 25°C by using an Ubbelohde capillary viscometer. From these results, reduced viscosity for film casting was calculated.

Preparation of PBA Films

The concentrations of PBA solution in chloroform used for film casting were 9, 12, 15, and 18 g/dL, respectively. The homogenized solution was poured into a stainless steel dish and dried to obtain films having thickness of 155 μm .

Zone Drawing of PBA Films

Zone drawing was carried out at several temperatures by moving a pair of narrow band heaters with dimensions in length of 7 cm, width of 2.5 cm, and thickness of 1 mm, as shown in Figure 1.

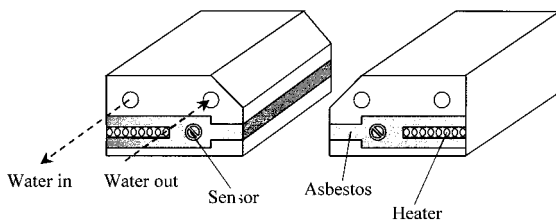


Figure 2 Schematic representation of the band heater assembly.

The film of 155 μm thickness, 1 cm width, and 10 cm length was drawn under tensions controlled by different dead weights on an Instron model 4201^{21,22,27–30} (Fig. 2). The zone drawing conditions are listed in Table I.

Characterization of PBA Films

Birefringence was measured on a polarizing microscope with a senarmont compensator (Nikon, Optiphot-Pol 104). It was determined by dividing the optical path length by the thickness.

Wide angle X-ray diffraction pattern was obtained by Statton camera with flat-plate geometry using Ni-filtered $\text{CuK}\alpha$ radiation at 40 kV and 45 mA. The pattern was recorded on a Kodak direct exposure film using pinhole collimation under vacuum. The exposure times for wide-angle X-ray diffraction was 12 h. Wide-angle X-ray diffractograms of PBA films for determinations of crystallinity were obtained in the range of 2θ of 5–65° at a scan speed of 1°/min. The crystallinity was calculated using a basic method for differentiation between crystalline and amorphous scatterings in diffraction intensity curves.³¹

Load–elongation curves were recorded on an Instron model 4201 using a sample length of 2 cm and a crosshead speed of 100 mm/min. The tensile strength and modulus of PBA films were the average values of 20 samples, respectively.

Hydrolytic biodegradations of PBA films having thickness of about 50 μm and draw ratios of about 4 were studied as follows: the film specimens were immersed in a vial containing 50 mM

Table I Zone Drawing Conditions of PBA Film

Drawing stress (MPa)	0.25, 0.50, 0.75, 1.00, 1.50, 3.00, 4.00, 5.00, 7.00
Drawing temperature (°C)	30, 40, 50, 60
Heat band speed (mm/min)	1, 5, 10, 20

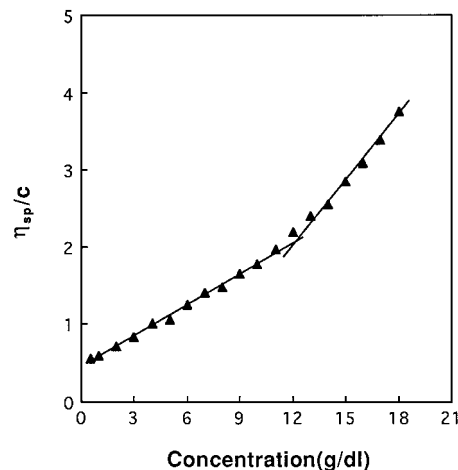


Figure 3 Reduced viscosity of PBA solution in chloroform at 25°C with solution concentration.

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.

RESULTS AND DISCUSSION

Determination of Optimum Polymer Concentration Using Viscosity and Drawability

The highest molecular orientation can be achieved by maximum drawing of a film cast at the concentration where a suitable amount of chain entanglements exists. In the vicinity of this concentration, the viscosity of solution increases steeply. Thus, in this study, relative viscosity was measured to determine the optimum solution concentration of PBA. All data were approximated to two different linear lines, as shown in Figure 3, and the critical polymer concentration of 12 g/dL was obtained where an abrupt change in viscosity was present. To confirm these viscosity data, we tried to optimum polymer concentration of the PBA solution by zone drawing method.

In general, the structure and physical properties of a zone-drawn film vary dependently with a degree of orientation, which is greatly affected by

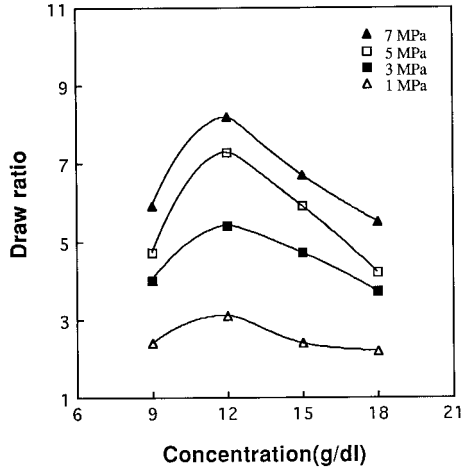


Figure 4 Zone draw ratio of PBA film drawn under various drawing stresses with concentration of PBA solution. Drawing temperature and heat band speed were 60°C and 1 mm/min, respectively.

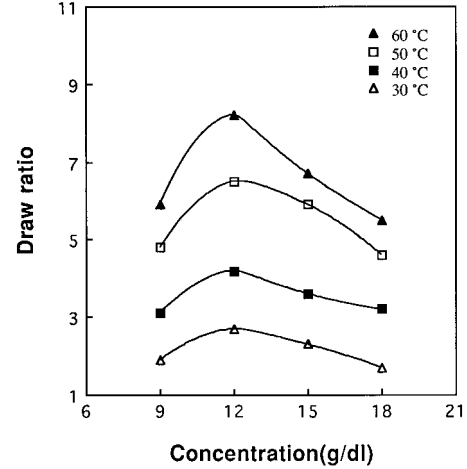


Figure 5 Zone draw ratio of PBA film drawn under various drawing temperatures with concentration of PBA solution. Drawing stress and heat band speed were 7 MPa and 1 mm/min, respectively.

a draw ratio. In the case of zone drawing, a draw ratio is governed by an initial concentration of polymer solution and by processing parameters for drawing such as drawing stress, drawing temperature, and heat band speed. Figure 4 shows the zone draw ratios of PBA films under various drawing stresses as a function of initial solution concentration, where drawing temperature was fixed at 60°C and heat band speed was 1 mm/min. The draw ratio increased with an increase in the drawing stress. Maximum value up to 8.2 was obtained at a drawing stress of 7 MPa. This result can be explained by the fact that deformation of molecular chains increases with increasing drawing stress above glass transition temperature. Under a drawing stress higher than 7 MPa, a breakage of film occurred. The maximum value of draw ratio appeared at the solution concentration of 12 g/dL.

In Figure 5, the zone draw ratios of PBA films drawn under various drawing temperatures as a function of the initial solution concentrations are presented. Drawing stress and heat band speed were 7 MPa and 1 mm/min, respectively. Draw ratio increased for each film with increasing drawing temperature. This implies that as drawing temperature reaches melting temperature (61°C) of undrawn PBA film, degree of freedom of PBA chains increases. The film obtained at the initial concentration of 12 g/dL had the maximum draw ratio.

The zone draw ratios of PBA films drawn under various heat band speeds as a function of the

initial solution concentrations are presented in Figure 6. Drawing stress and drawing temperature were 7 MPa and 60°C, respectively. It was shown that the slower the heat band speed, the larger the draw ratio. This can be explained by the fact that a softening of film is easier, owing to longer residence time for film between two heat bands. That is, more uniform heat transfer to the sample, which is achieved by a slower heat band speed, had a greater effect on the draw ratio of the PBA film. As identified in Figures 4, 5, and 6, the zone draw ratio of a film prepared at the concen-

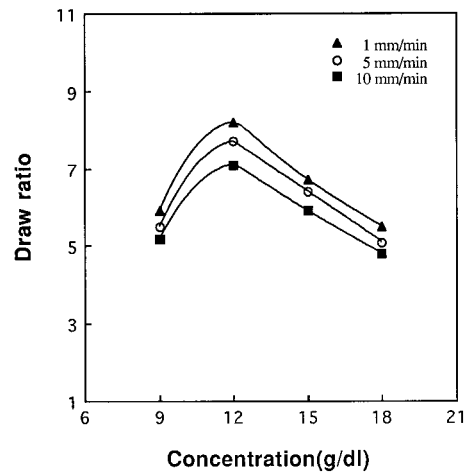


Figure 6 Zone draw ratio of PBA film drawn under various heat band speeds with concentration of PBA solution. Drawing stress and drawing temperature were 7 MPa and 60°C, respectively.

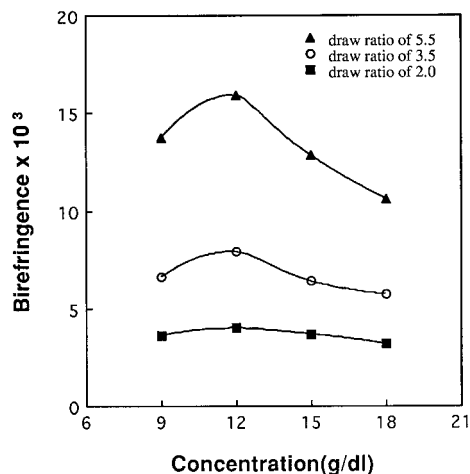


Figure 7 Birefringence of PBA film zone drawn under various drawing stresses as a function of draw ratio. Drawing temperature and heat band speed were 60°C and 1 mm/min, respectively.

tration of 12 g/dL was the largest among those of the films cast at different concentrations. Thus, it was supposed that the film prepared at this concentration have suitable entanglements to attain maximum draw ratio. Conclusively, it can be predicted that the present method determining optimum initial concentration of PBA solution by zone draw ratio is correct and suitable.

Effect of Initial Concentration and Draw Ratio on the Physical Properties of the Film

The effect of the initial polymer concentration on the birefringences of the PBA films with different draw ratios is presented in Figure 7. The draw ratio was controlled by varying drawing stresses under the same drawing temperature of 60°C and heat band speed of 1 mm/min. It is interesting that the concentration effect is obvious at the same draw ratio. The maximum birefringence appeared at the solution concentration of 12 g/dL, whereas at lower or higher concentrations, birefringence decreased. This demonstrates that the overall orientation of the PBA film cast at 12 g/dL is the highest among those cast at other concentrations. As displayed in Figure 8, wide-angle X-ray diffraction photograph of the PBA film having draw ratio of 3.5 prepared at the initial concentration of 12 g/dL indicates that high degree of orientation was achieved. Consequently, it is well suggested that a suitable amount of entanglement facilitates the orientation of polymer chains along the drawing direction.

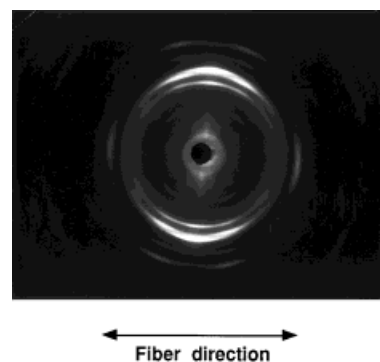


Figure 8 Wide-angle X-ray diffraction photograph of one-step zone-drawn PBA film prepared at the initial concentration of 12 g/dL. Draw ratio was 3.5.

Figure 9 presents the crystallinities of PBA films with different draw ratios as a function of initial concentration. Drawing condition was the same as described in Figure 7. As draw ratio increased, crystallinity increased at all polymer concentrations. This result agreed well with the previous draw ratio and birefringence data. However, interestingly, the crystallinities of the zone-drawn PBA films having the same draw ratio were nearly constant, irrespective of initial polymer concentrations.

The influence of the initial concentration of polymer solution on tensile strength (a) and tensile modulus (b) of the PBA films was examined. The same zone drawing condition as described in Figures 7 and 9 was applied. As shown in Figure

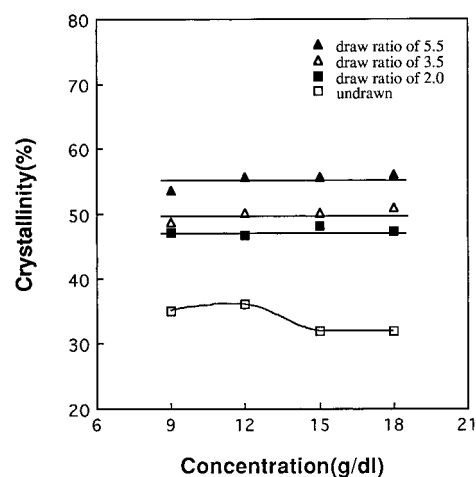


Figure 9 Crystallinity of PBA film zone drawn under various drawing stresses as a function of the draw ratio. Drawing temperature and heat band speed were 60°C and 1 mm/min, respectively.

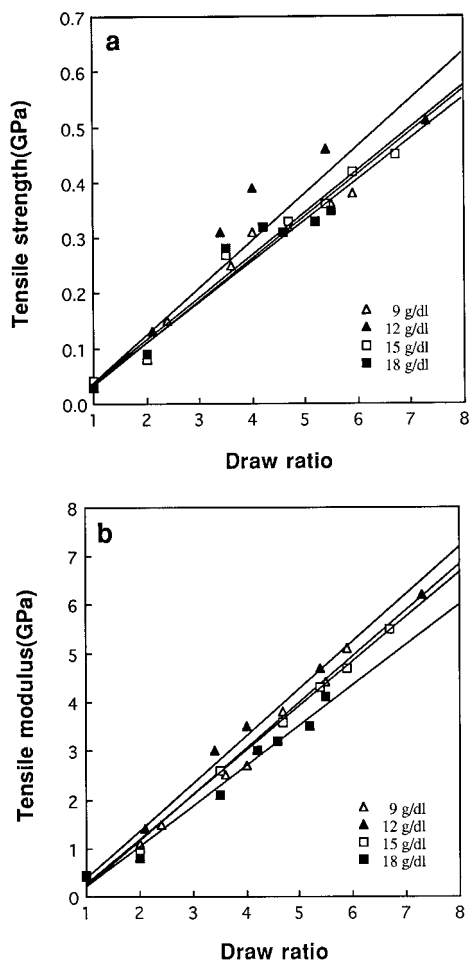


Figure 10 Tensile strength (a) and tensile modulus (b) of PBA film zone drawn under various drawing stresses as a function of draw ratio. Drawing temperature and heat band speed were 60°C and 1 mm/min, respectively.

10, the tensile properties of PBA film increased significantly with the draw ratio. Notably, the maximum strength of 0.59 GPa and modulus of 7.8 GPa were obtained at 12 g/dL concentration. It was observed that the film having the optimum macromolecular entanglements at the concentration of 12 g/dL represented the highest drawability, degree of orientation, tensile strength, and tensile modulus. In general, the fact that the film represents high tensile strength and tensile modulus may imply that the polymer has the suitable length of tie molecules and uniform length distribution. The PBA film cast at 12 g/dL represented higher tensile strength and tensile modulus than the PBA films cast at other concentrations because the film had suitable tie molecules and uniform length distribution. The PBA films cast at

lower concentrations had fewer tie molecules, so tensile strength and tensile modulus were lowered due to slippage of molecular chains.

Effect of Initial Concentration on the Biodegradability

In this study, to precisely clarify the effects of the initial polymer concentration, orientation, and crystal morphology on the microbial and hydrolytic degradations of the PBA film, we used the PBA films with the same draw ratios of 3.5, the same film thicknesses of 50 μm , and the similar degrees of crystallinities of 59–61% in biodegradability test. Figure 11 shows the results. The degradation rate was greatly affected by the initial polymer concentration. That is, the degradation rate of the PBA films at 12 g/dL having the highest orientations was lowest, despite nearly the similar crystallinities of all films used. From these results, it is concluded that the chain orientation obtained by fine control of the initial polymer concentration and the zone-draw ratio has a marked influence on the biodegradability of the PBA film.

CONCLUSIONS

Biodegradable PBA films with various physical properties were produced by control of initial polymer concentrations and zone drawing conditions. The optimum processing condition for the

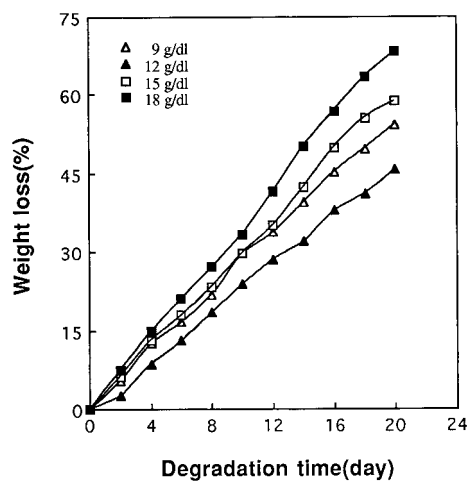


Figure 11 Degradation profile of one-step zone-drawn PBA films of ca. 50 μm thickness prepared at four different initial concentrations. Draw ratio was fixed at ca. 3.5.

biodegradable PBA film was investigated by measuring the birefringence, degree of orientation, crystallinity, tensile properties, and biodegradability. PBA films were prepared from chloroform solutions with different initial concentrations of 9, 12, 15, and 18 g/dL, respectively. To investigate the drawing behavior of the PBA films with different solution concentrations, the films were drawn under various zone drawing conditions. From the several results, it was identified that the concentration of PBA in chloroform caused significant changes in the draw ratio of the PBA film. That is, the maximum zone draw ratio and the maximum tensile properties were observed at the initial concentration of 12 g/dL for the drawn PBA films; the draw ratio of 8.2, the tensile strength of 0.59 GPa, and the tensile modulus of 7.8 GPa were obtained, respectively. Moreover, crystal and amorphous orientations and tensile properties of the PBA film at 12 g/dL were the highest among the films cast at five different initial polymer concentrations under the same draw ratio and the same crystallinity. It was identified that these physical properties described above had a marked influence on the biodegradability of the PBA film. Conclusively, it is possible to produce various PBA films having different physical properties and biodegradabilities at different initial polymer concentrations by adopting a simple zone drawing method. In the near future, we will report on the comparison of the biodegradation behaviors of the PBA films having various structures and physical properties prepared by our zone drawing and general hot drawing methods, respectively.

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