Characterization and processing of Biodegradable polymer blends of poly(lactic acid) with poly(butylene succinate adipate)

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Abstract

We investigated thermal, rheological, morphological and mechanical properties of a binary blend of poly(lactic acid) (PLA) and poly(butylene succinate adipate) (PBSA). The blends were extruded and their molded properties were examined. DSC thermograms of blends indicated that the thermal properties of PLA did not change noticeably with the amount of PBSA, but thermogravimetric analysis showed that thermal stability of the blends was lower than that of pure PLA and PBSA. Immiscibility was checked with thermal data. The rheological properties of the blends changed remarkably with composition. The tensile strength and modulus of blends decreased with PBSA content. Interestingly, however, the impact strength of PLA/ PBSA (80/20) blend was seriously increased higher than the rule of mixture. Morphology of the blends showed a typical sea and island structure of immiscible blend. The effect of the blend composition on the biodegradation was also investigated. In the early stage of the degradation test, the highest rate was observed for the blend containing 80 wt% PBSA.

Keywords : poly(butylene succinate adipate), poly(lactic acid), biodegradable, BOD5

1. Introduction

In recent years, much concern has increased on the deterioration of our environment due to solid waste pollution. One way to solve that problem is replacing commodity synthetic polymers with biodegradable polymers. Among them, aliphatic polyester is one of the most promising biodegradable materials because they are readily susceptible to biological attack (Huang, 1985).

PLA, a biodegradable aliphatic polyester, produced from renewable resources has received much attention in the research of alternative biodegradable polymers (Tsuji and Ikada, 1998; Perego *et al.*, 1996). Lactides and lactic acid monomers are obtained from the fermentation of crop like corn starch and sugar feed stocks (Lunt, 1998). Polymerization of lactic acid into PLA produces a biodegradable thermoplastic polyester with good biocompatibility and physical properties, such as high mechanical strength, thermoplasticity and fabricability (Cai *et al.*, 1996). PLA has mostly been used for biomedical applications such as drug delivery systems (Schwacch and Coudance, 1995) and controlled release matrices for fertilizers, pesticides and herbicides. Despite its good properties, the applications are limited due to its low flexibility and low impact strength. To improve the flexibility and the impact strength of PLA, blending (Liu *et al.*, 1997; Grijpma *et al.*, 1994; Zhang *et al.*, 1998; Nijenhuis *et al.*, 1996), copolymerization and reactive extrusion techniques were used. Some of these blends were found to be immiscible, resulting in poor mechanical properties.

PLA is an aliphatic polyester with one of the highest melting temperatures of at around 160~180°C. Generally a polymer having a lower melting temperature is more susceptible to biodegradation than one having a higher melting temperature (Tokiwa and Suzuki, 1981) because it has more flexible chains which can fit into the active sites of enzymes. On the other hand, PBSA is commercially available aliphatic polyester with high flexibility, excellent impact strength, melt processibility, thermal, chemical resistance (Mayer and Kaplan, 1994; Nishioka *et al.*, 1994) and low melting point of 90°C, which is more readily biodegraded than PLA. Many studies on PBSA, in the form of films and molded objects, have exhibited siginificant biodegradation within several months in soil, water with activated sludge, and sea water (Nishioka *et al.*, 1994).

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Thus, our research focuses on the addition of PBSA to PLA as a blend with improved impact property, while maintaining biodegradability and processibility.

In this study, we have prepared PLA/PBSA blends to obtain biodegradable polymers with good impact resistance and investigated various aspects of the thermal, rheological, and mechanical properties in these blend systems.

As a result of blending PLA with PBSA, it is expected to be fully biodegradable since the individual components are biodegradable. The biodegradation rate of PLA was accelerated and the impact strength much improved over pure PLA.

2. Experimental

2.1. Materials

Fiber grade PLA (Nature work 6200D, Mw = 147 k) produced by Cargil-Dow Co. were used and a biodegradable co-polyester, PBSA (SG200, Mw = 60 k), supplied from SK Chemicals Co. The chemical structures of PLA and PBSA are shown in Scheme 1.

2.2. Blend preparation

The pellets of PLA and PBSA were dried in a vacuum oven at 50°C for at least 12 hours before use. PBSA contents were 0, 10, 20, 40, 60, 80 and 100 wt%. Blends were made as follows. Dried pellets of PLA and PBSA were mixed in a container before blending in a co-rotating twin screw extruder (Collin Techline ZK257) at a fixed rotation speed of 30 rpm. The extrusion temperatures of the feeding zone/melting zone/metering zone/die were set at 90~100/ 170~180/170~180/170~180°C. Specimens of blended samples were obtained by compression molding after drying at 50°C for at least 12 hours under vacuum. The molding temperatures were 130°C, 200°C, and 180°C for PBSA, PLA, and the blends, respectively.

2.3. Instruments

**Thermal properties.** Differential scanning calorimetric studies for the thermal property characterization were performed on a modulated DSC (TA Instrument Model 2910). The heating rate and the cooling rate were 20°C/min and 5°C/min, respectively. Every thermogram was repeated at least twice, and a duplicate blend was then analyzed to verify the reproducibility of the measurement. The thermal stabilities of the blends were measured by thermogravimetric analysis (TGA, TA Instruments Model 2950) in a nitrogen atmosphere at a heating rate of 20°C/min.

Rheological properties. Rheological properties of the blends and pure resins were measured using a ARES (ARES, TA Instrument) on which a 25 mm diameter parallel plate was mounted. The frequency range was set at 0.1~500 rad/sec and the applied strain was 10%. The plate gap was set at 1.2 mm. Before the measurement, the samples were prepared using compression moulder at 200°C. Measurements were done under nitrogen atmosphere.

Mechanical properties. Testing of the mechanical properties of the blends was done using Universal Testing Machine (Lloyd Instruments, LR5K plus). A gauge length of 25.4 mm and a crosshead speed of 50 mm/min were used. Impact testing was done using a pneumatic driving instrumented impact tester (Ceast Model 6545) in Izod mode with a notch of 2.54 mm according to ASTM D256. All the reported results are also averages of at least ten measurements for each blending system.

Morphology. Scanning electron microscopy (SEM) observations of the blended samples were performed on Hitachi model S-2200C. The samples, fractured during impact test, were coated with gold to make them electrically conducting.

Biodegradability. As a biodegradation study, biological oxygen demand (BOD5) analysis was made by means of WTW Oxytop-C unit thermostatted at 20°C. The extent of biodegradation was quantified as the pressure drop and was converted to the oxygen consumption daily during the experiment. The activated sludge from an industrial waste water treatment plant was aerated for 24 hours before use. Cellulose was also tested for comparison.
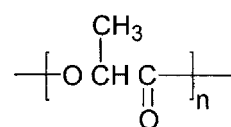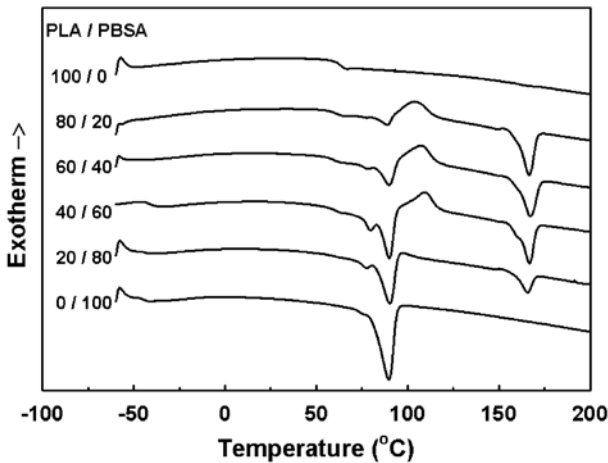

PLA (6200D)
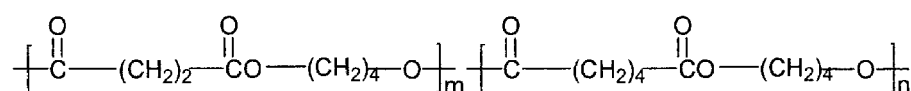
PBSA (SG200)

Scheme 1

Fig. 1. DSC thermograms of PLA/PBSA blends (the second heating, heating rate: 20°C/min).

3. Results and discussion

3.1. Thermal properties

The results of DSC heating scans for the PLA/PBSA blends were presented in Fig. 1. They showed two endothermic peaks for the second heating. Thermal properties of the blends were summarized in Table 1.

The glass transition temperatures (T_g) of the PBSA and the PLA were about −45°C and about 63°C, respectively. A direct proof of polymer miscibility in blend can be obtained by observing the behavior of the T_g with the blend composition. Increasing PBSA contents in the blends resulted in two different behaviours. The higher T_g decreased from 63°C for pure PLA to 59°C for blend containing 80 wt% PBSA due to active interaction between PLA and PBSA chains. This could be an indication of partial miscibility of the two polymers. On the other hand, the lower T_g of the blend showed slightly higher value than that of pure PBSA, which was found to slightly increase with increasing PLA content.

The melting temperature of PLA was around 164°C but that in the blend jumped up to 167°C at 40 wt% PBSA contents and slightly decreased at more than 40 wt% PBSA contents. No accurate heat of fusion of PBSA and heat of re-crystallization of PLA could be determined for the blends due to overlap of the melting endotherm and the re-crystallization exotherm.

Fig. 1 also shows the exothermic peaks which are attributed to crystallite reorganization during heating. These newly formed crystallites melted on continuous heating. The re-crystallization temperature (T_{rc}) of PLA increased with increasing PBSA content. Re-crystallization of the initially amorphous PLA fraction can take place only at temperatures above T_g, where the mobility of the PLA chain is sufficiently high to reorganize into a new crystalline conformation. However, pure PLA does not show any apparent re-crystallization peak. This behavior is very similar to typical plasticized thermoplastics (Schwacch and Coudance J., 1995), where plasticizers may promotes crystallinity due to enhanced chain mobility and the addition of PBSA also favored crystallization around 110°C. This means that PBSA can be regarded as an efficient plasticizers of PLA.

The theoretical ΔH_m values for PBS (polybutylene succinate) and PBA (polybutylene adipate) are 110.3 and 135.0 J/g, respectively, calculated on the basis of the group contribution method proposed by Van Krevelen(Van Krevelen, 1990). However the experimental value of that for PBSA was only 42 J/g. This difference may be due to the copolymer structure of PBSA.

Co-polyester PBSA shows double endothermic peaks in the DSC curve for the second heating. These peaks are attributed to re-melting of newly formed crystallite during heating (Roberts, 1970; Sweet and Bell, 1972). Crystallites of poor quality and with low melting temperature re-crystallize to crystallites with higher melting temperature when low heating rates are employed. The reason for the appearance of double endothermic peaks in the second heating scan is probably due to quenching after the first heating which does not give enough time for high melting crystallite to form, so more low melting crystallite are produced.

Interestingly, the pure PLA showed a clear glass transition temperature and a very small melting endotherm at around 164°C, corresponding to residual crystallinity due to its very slow rate of crystallization.

The crystallization behavior of the blends was also checked through dynamic crystallization from the melt and is presented in Table 1. The crystallization temperature (T_c)

Table 1. Thermal properties of PLA/PBSA blends

PBSA (wt%)	T_g(°C)		T_m(°C)		T_{rc}(°C)	ΔH_m(J/g)		T_c(°C)	ΔH_c(J/PBSA g)
	PBSA	PLA	PBSA	PLA	PLA	PBSA	PLA	PBSA	PBSA
0	-	62.7	-	164.3	-	-	0.4	-	-
20	-	60.1	89.0	166.7	104.4	-	28.6	63.1	31.7
40	-44.1	59.3	89.8	167.3	108.0	-	22.0	63.0	36.0
60	-44.4	59.0	90.0	166.8	109.6	-	14.9	62.9	36.1
80	-44.7	58.7	90.2	165.6	-	-	9.2	61.9	37.9
100	-45.0	-	89.7	-	-	46.9	-	61.5	45.6

of PBSA were slightly increased with increasing PLA content but the heat of crystallization (ΔH_c) of PBSA per unit mass of PBSA was decreased. This indicates that the degree of crystallinity of the blends was decreased with the addition of PLA at cooling rate of 5°C/min. This may be due to slow movement of PLA chain with higher glass transition temperature. For pure PLA, on the other hand, no exothermic peak could be observed in the cooling run of PLA at 5°C/min. Upon cooling from 200°C, only a base line change with T_g appears at 60°C. Miyata and Masuko (Miyata and Masuko, 1998) also obtained similar results and concluded that in their experiment, the PLA film cooled from the isotropic melt a rate greater than 10°C/min remained amorphous. Liu *et al*. (Liu *et al*., 1997) discussed about the crystallization behavior of PLA and the crystallinity could be obtained after annealing at 105°C for 90 min. It means that PLA product obtained from conventional plastic processing may be nearly amorphous due to its slow crystallization rate (Martin and Averous, 2001).

Table 2 summarizes the results of thermogravimetric analysis (TGA) for PLA/PBSA blends under nitrogen atmosphere. Decomposition onset temperature defined as the temperature at 1% weight loss was decreased until when the PBSA content was around 50 wt%. It appears that the maximum instability occurs at this composition.

With the assumption of first order decomposition reaction, the thermal decomposition activation energy (E_a) of the blends at the moment of initial decomposition was calculated as shown in Table 2. Although there was small deviation, the decomposition activation energy of blends was about 126~127 kJ/mol when the PBSA content was 20 ~40 wt%, it was about 150~151 kJ/mol when the PBSA content was 60~80 wt%, and it was about 87~89 kJ/mol for pure PLA and PBSA.

This indicates that the PLA/PBSA blends have an effect on the acceleration of thermal decomposition and this may be due to the thermal energy transfer between the matrix and dispersed phase. The frequency factor also showed a similar behavior to activation energy.

3.2. Rheological properties

Fig. 2 shows the complex viscosities of PLA/PBSA blends as a function of frequency at 200°C. The general
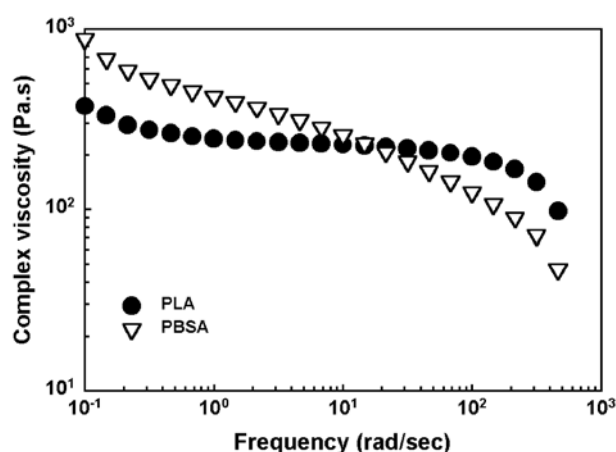
Fig. 2. Complex viscosity vs. frequency for pure PLA and pure PBSA at 200°C.

behavior of the blends follows that of typical thermoplastic polymers, i.e. near Newtonian behavior at low shear rate and shear-thinning at high shear rate. The complex viscosities of PLA followed the general behavior but those of PBSA showed shear thinning behavior even at the low frequencies (10^{-1} to 10^0 rad/sec). The viscosities of PLA were much lower than those of PBSA at low frequencies but it reversed at high frequency. Two factors from the rheological point of view should be taken into consideration to obtain a polymer blend with good mechanical properties. The first is that the viscosity ratio of the dispersed phase to the matrix phase should be less than 1 for stable morphology. The second factor is that it should be close to 1 for good dispersion (Wu, 1985). From Fig. 2, the viscosity ratio of PLA/PBSA blends is nearly 1 around the frequency of 20 rad/sec, which means that the blend processed at around the shear rate of 20 may have the most uniform dispersion.

3.3. Mechanical properties

Fig. 3 shows the tensile strength of the blends versus PBSA content. The tensile strength decreased at up to 80 wt% PBSA contents and slightly increased at more than 80 wt% PBSA contents. This kind of results that the tensile strength values are below the line of rule of mixing could

Table 2. Dynamic thermogravimetric data of PLA/PBSA blends

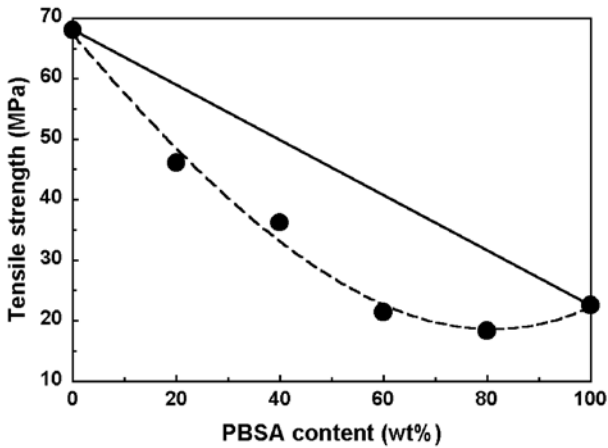| PBSA (wt%)	Decomposition onset temperature(°C)	Maximum decomposition temperature(°C)		Activation energy, E_a(kJ/mol)	Ln (pre-exponential factor), ln A(min^{-1})
		PLA	PBSA		
0	345.2	414.7	-	87.0	11.5
20	317.7	402.8	434.2	126.5	20.9
40	309.9	393.1	443.8	125.8	21.0
60	309.5	367.7	444.3	150.2	26.5
80	316.0	360.9	445.0	151.2	26.3
100	333.4	-	445.3	89.4	12.5

Fig. 3. Tensile strength vs. PBSA content for PLA/PBSA blends.
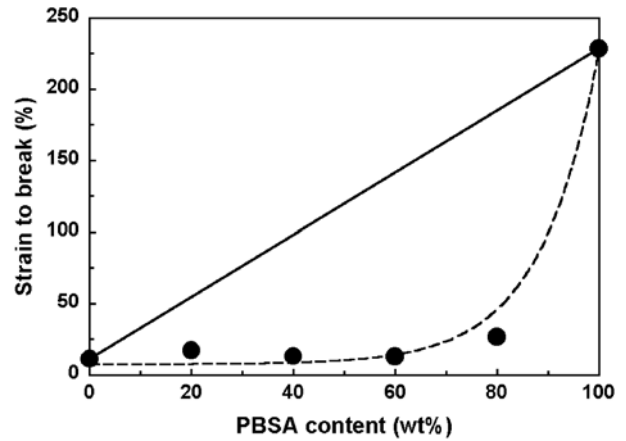

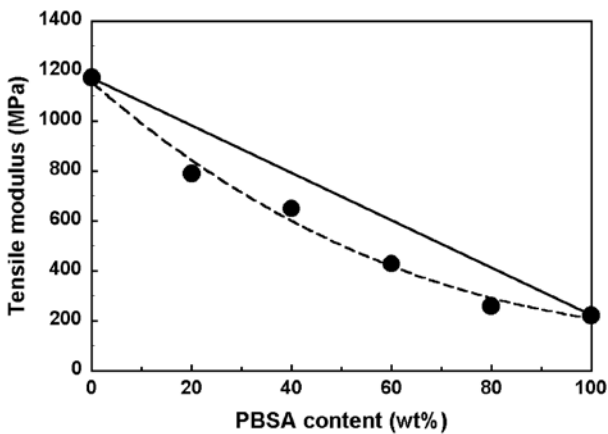**Fig. 5.** Strain to break vs. PBSA content for PLA/PBSA blends.

Fig. 4. Tensile modulus vs. PBSA content for PLA/PBSA blends.
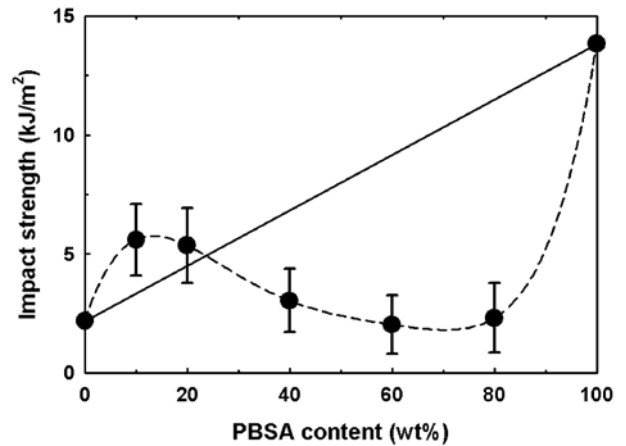

Fig. 6. Impact strength vs. PBSA content for PLA/PBSA blends.

be seen in typical immiscible polymer blends. The tensile modulus also shows a similar behavior to tensile strength (Fig. 4). The strain to break as a function of PBSA contents is shown in Fig. 5. As PBSA contents increased, the strain to break was nearly constant up to 60 wt% PBSA content and rapidly increased at more than that composition. This may be attributed to the much more elastic characteristic of PBSA matrix phase.

For the PLA sample, no yield phenomenon existed; for the PLA/PBSA (80/20) blend, the specimens broke rapidly after yield; for the pure PBSA, after necking, the stress increased with strain above the yield stress.

Impact strength of PLA/PBSA blends with PBSA contents was shown in Fig. 6. Interestingly, we could observe that when PBSA content is at 10~20 wt%, the impact strength of the blends showed much higher value than the line of mixing rule even though at higher composition, it was much lower than the line. Like a typical rubber toughening system, a remarkable improvement of about two and half times of pure PLA in impact strength can be realized by using only 10~20 wt% PBSA in PLA.

3.4. Morphologies

SEM micrographs of fractured surfaces prepared at impact test show the morphology of binary blends of PLA/PBSA as given in Fig. 7. In Fig. 7(a), the dispersed phase of PBSA particles were relatively small, the mean diameter of 1.2 μm. Due to the increase of PBSA content, the particle size became larger (Fig. 7(b)), the mean diameter of 4 μm. Above 50 wt% PBSA content, the morphology inversed and PLA and PBSA became domain and matrix, respectively. The particle size of PLA in Fig. 7(d) showed slightly smaller, the mean diameter of 0.8 μm than that of PBSA in Fig. 7(a). It may be due to the fact that PBSA is more viscous than PLA at low shear rate shown in Fig. 2. This indicates the traditional morphology of immiscible blend system.

3.5. Biodegradability

PLA/PBSA blends and cellulose were biodegraded with activated sludge by an Oxytop-C unit. In this study, the PLA and PBSA were found to exhibit oxygen consumption of about 11 ppm and 17 ppm after 5 days at 20°C,
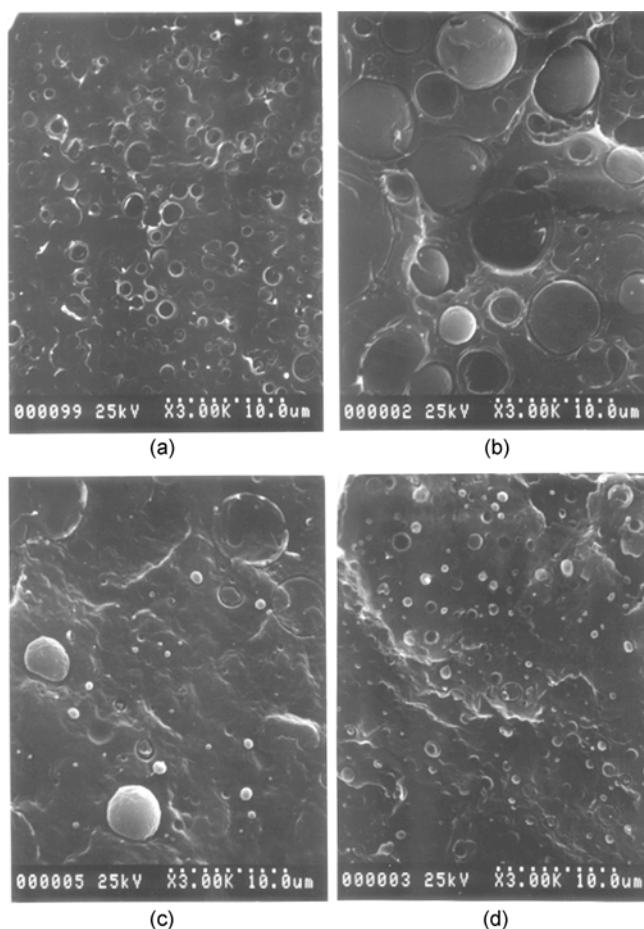
Fig. 7. SEM photographs of impact fractured surfaces of PLA/ PBSA blend: (a) 80/20 (b) 60/40 (c) 40/60 (d) 20/80.
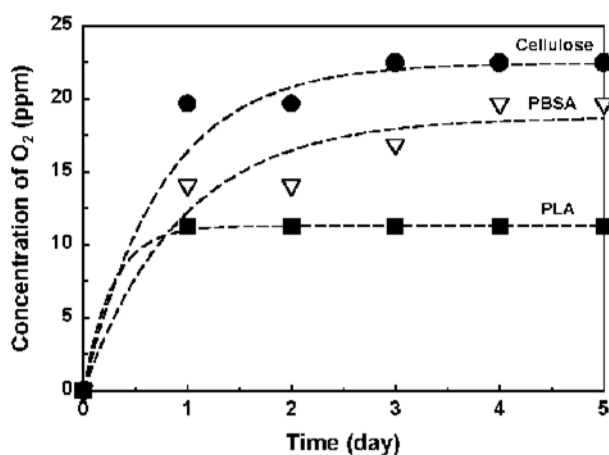

Fig. 8. Concentration of O$_2$ vs. time for PLA, PBSA and cellulose.

respectively (Fig. 8). At the first day, oxygen consumption of the blends increased as PBSA content increased up to about 80 wt% PBSA contents and decreased more than that as shown in Fig. 9. On the other hand, at the fifth day,
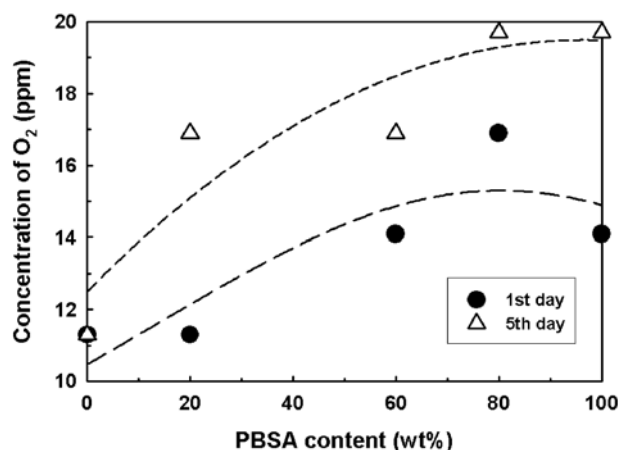

Fig. 9. Concentration of O$_2$ vs. PBSA content with time.

the maximum point of oxygen consumption moved toward higher PBSA content.

The faster degradation of the blends than pure components may be due to more space in the immiscible blends so that microorganisms more easily begin to degrade blends and more oxygen consumption is obtained.

4. Conclusions

Blends of PLA (6200D) with PBSA (SG200) were studied. The blends were extruded and their molded properties were examined. Since these two polymers are incompatible, their behaviors, in general, follow that of incompatible polymer blends. The study of thermal properties revealed that the T$_g$ of PLA in the blends was slightly decreased with increasing PBSA content, and stability of the blends at high temperature was lower than that of pure PLA and PBSA. The tensile strength and tensile modulus of the blends were decreased with PBSA content. Interestingly, however, at 20 wt% PBSA content, the impact strength increased much higher than pure PLA as can be seen in a toughening system. The biodegradation rate of the blends showed the highest at the blend containing 80 wt% PBSA in the early stage.

The PLA and PBSA used in this study are immiscible. Partial miscibility of the dispersed phase with the matrix can bring about many property changes, including tensile properties. We feel that this should be examined further to improve the mechanical properties of the PLA/PBSA system. Three different methods can be applied for this purpose. The first is functionalization at the dispersed phase surface, the second is the addition of the compatibilizer and the third is the in-situ compatibilization. This study is under way and will be reported in the near future.

Acknowledgements

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