Macromol. Symp. **2003**, *197*, 65–76

Thermal and Mechanical Properties of Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) Plasticized by Biodegradable Soybean Oils

*Jea Shin Choi, Won Ho Park**

Department of Textile Engineering, College of Engineering, Chungnam National University, Taejon 305-764, Korea
Fax : +82-42-823-3736; E-mail: parkwh@cnu.ac.kr.

Summary: The effects of soybean oil (SO) and epoxidized soybean oil(ESO) as biodegradable plasticizers for poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) were studied using thermal and mechanical analyses. PHBV/SO and PHBV/ESO blends were prepared by evaporating solvent from blend solutions. The levels of additive in the blend varied from 5% to 30%. As a plasticizer for PHBV, ESO was more effective than SO in depression of the glass transition temperature as well as in increasing the elongation at break and the impact strength of the films with increasing levels of additive. Biodegradation of the plasticized PHBV films was carried out by accelerated compost method. The degradation rates of the blend films with SO or ESO were found to be faster than that of PHBV film. From the thermogravimetric analysis, it was found that the thermal reaction between the epoxide groups of ESO and PHBV fragments with carboxylic chain ends, occurred during the degradation of PHBV/ESO blends.

Keywords: additive; blend; epoxidized soybean oil; plasticization; poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

Introduction

Poly(3-hydroxybutyrate) (PHB), which is biosynthesized by a wide variety of bacteria, is a biodegradable thermoplastic with biocompatibility and ecological safety. Therefore, it has much potential in applications such as surgical sutures, long-term carriers for drugs, and degradable plastics. However, until now there are no large commercial products because PHB has higher cost, narrow processability window and brittleness, than commercial synthetic polymers. These drawbacks in PHB can be overcome by internal or external plasticization to improve impact strength, elongation at break and ductility.

From many attempts for the internal plasticization of PHB, various copolymers with 3-hydroxyvalerate[1-3], 4-hydroxybutyrate[4-6], and 3-hydroxyalkanote units[7-9] have been

DOI: 10.1002/masy.200350707

developed using the bacterial fermentation method. These copolymers have improved physical and mechanical properties, compared to PHB homopolymer.

On the other hand, the external plasticization is more efficient to apply to polymers because it could provide a relatively simple route to improve some physical properties of polymer as well as a lower cost for products. However, plasticizers for biodegradable polymers should preferably also be biodegradable. In this respect, most of plasticizers used in synthetic polymer processing are not suitable for PHB. There was only a few reports10-13) on the external plasticization of PHB, though biodegradable plasticizers play an important role in the practical processing for some applications such as packaging materials.

In the previous studies14,15), we found that additives with epoxide pendant groups could improve the thermal stability of PHB in their blends. The objective of this study is to develop the appropriate plasticizer with epoxide groups for improving the stiffness and thermal stability of PHB. We focused on the comparison of physical and mechanical properties of PHB blends, plasticized by either soybean oil or epoxidized soybean oil at varying levels of oil content.

Experimental Part

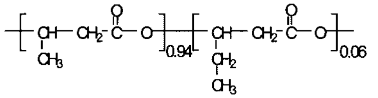
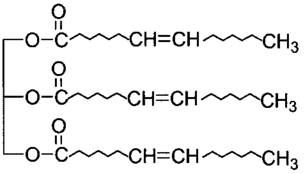
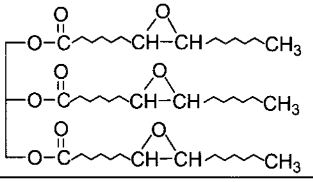
Materials

The PHBV sample, as an injection-molding grade in chip form, used in the present work was kindly supplied by Zeneca Co. The PHBV copolymer consisted of 94% of 3-hydroxybutyrate unit and 6% of 3-hydroxyvalerate unit, as determined by ^{1}H NMR analysis by using a Bruker AC-200 NMR spectrometer. Soybean oil (SO) was purchased from Aldrich Co. and epoxidized soybean oil (ESO) with epoxide content of 6.9 wt% was supplied by Shindongbang Co. Epoxide content (6.9 wt%) of ESO indicates that approximately 95% of unsaturated groups in SO was epoxidized.

Preparation of PBH/additive blends

PHBV/additive blends (100/0, 95/5, 90/10, 80/20, 70/30, w/w) were prepared by evaporating chloroform from polymer/additive mixed solution (3 wt%) with pre-determined weight ratios. The resulting precipitates were dried *in vacuo* at 30°C. Chemical structure, molecular weight, and melting temperature of polymer and soybean oils are shown in Table 1.

Table 1. Chemical structure, molecular weight and melting temperature of PHBV and soybean oils

	Chemical structure	**M_W**	**T_m(°C)**
PHBV		680,000	161.0
SO		814.3	-30.4
ESO		872.2	-15.7

Characterization

^1H NMR spectra were obtained with a Bruker AC-200 NMR spectrometer. Chloroform-*d* solutions of the polymer at concentration of 10 mg/ml were analyzed. Differential scanning calorimetry (DSC) was conducted using a TA Instruments 2920 (DuPont Co.), calibrated with standards. Samples were heated from 20°C to 190°C at a rate of 10°C /min (first heating) and held at final temperature for 1 min to eliminate the thermal history applied to the samples. After cooling to -100°C, they were then reheated to 200°C at a rate of 10°C /min (second heating). Thermal parameters such as glass transition temperature (T_g), melting temperature (T_m), and cold-crystallization temperature (T_c) were obtained from second run. Thermogravimetric analysis (TGA) was conducted using a TA Instruments 2910 (DuPont Co.) in nitrogen atmosphere from 30 to 500°C at a heating rate of 20°C /min. Tensile properties of the dumbbell-shaped PHBV blend samples were carried out according to ASTM D638-5 on a Instron (Model 1137) at a crosshead speed of 5mm/min. Impact strength of the notched samples was obtained according to ASTM D256. The samples for impact test were injection-molded at 190°C by a Mini-Max molder using the solution-blended films.

Cryogenic fracture surfaces of the blend films were examined by scanning electron microscopy (SEM) (ISI-SX-40, Akashi Co.) with an accelerating voltage of 15kV. The samples for SEM observation were selectively etched in methanol for 1 hr at room temperature.

Composting Biodegradation Tests

Biodegradation of PHBV and its blend films was carried out in a simulated municipal solid waste aerobic composting test.[16)] The simulated waste consisted of 39.8% food waste, 20.7% shredded computer and news paper, 5.3% saw dust, 7.3% glass beads, 7.7% plastics, 4.5% rubbers, and 14.7% leaves. The reactor with the composting mixture was kept at pH 7 and 55°C with 60% moisture content. The tested samples were exposed to compost for 20 days. The biodegradation of these samples was expressed in terms of the residual weight of sample films.

Results and Discussion

Plasticizing Effect of Additives on PHBV

To investigate plasticizing effects of two soybean oils (SO, ESO) on PHBV, DSC was carried out using the PHBV blends with various additive content. Figure 1 shows the variations in glass transition temperature (T_g) obtained from the 2nd scan DSC thermograms of PHBV and its blends with ESO or SO at contents up to 30wt%. A decreasing trend of glass transition temperatures was observed in PHB/ESO blends, while this trend was not detected for PHB/SO blends. Therefore, ESO was expected to be miscible with PHB and improve the mobility of PHB molecular chains in the amorphous phase, indicating ESO acts as plasticizer. The T_c, T_m and ΔH_m thermal properties of PHB/additive blends, obtained from the second heating, are summarized in Table 2. The T_m value and normalized heat of fusion of PHBV did not change with increasing additive content, while the cold crystallization temperature (T_c) increased gradually with increasing additive content.

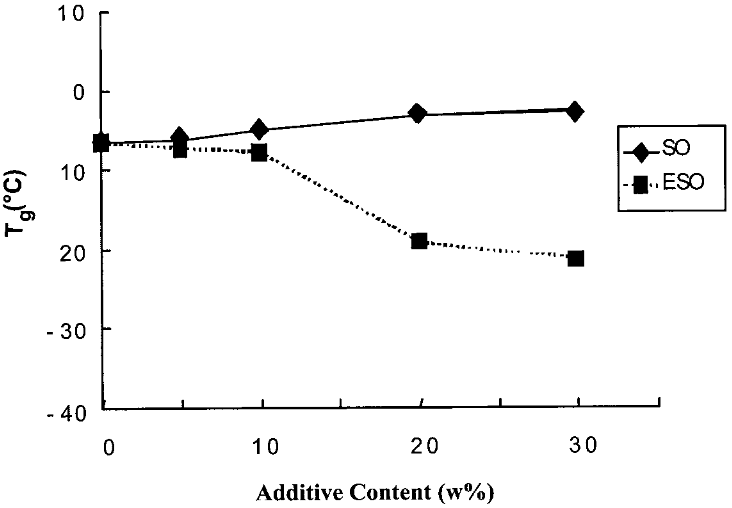


Figure 1. Glass transition temperature (T_g) of PHBV blends as a function of additive content.

Table 2. Thermal parameters of PHBV/additive blends

		T_c(°C)	T_m(°C)	ΔH_m(J/g)
PHBV		28.5	161.0	65.9
PHBV/SO	**95/5**	36.6	160.5	56.1
	90/10	39.6	158.2	58.1
	80/20	41.7	161.6	64.5
	70/30	48.7	158.9	67.0
PHBV/ESO	**95/5**	36.2	160.5	63.6
	90/10	34.8	160.3	68.0
	80/20	39.0	159.5	61.6
	70/30	41.6	159.6	56.3

Mechanical Properties of PHBV/Additive Blends

In order to ascertain if the brittleness of PHBV could be improved by blending with soybean oils, the tensile properties of PHBV were compared with those of PHBV/ESO and PHBV/SO blends. Strength, modulus and elongation at break of PHBV and its blends are shown in Table 3.

Table 3. Mechanical properties of PHVB/additive blends

		Tensile strength(kgf/mm^2)	**Tensile modulus (kgf/ mm^2)**	**Elongation at break (%)**
PHBV		2.6 (0.13)[a]	46.8 (2.88)	5.3 (0.50)
PHBV/SO	**95/5**	2.2 (0.09)	37.3 (4.40)	5.2 (0.54)
	90/10	1.4 (0.15)	36.5 (1.93)	4.3 (0.52)
	80/20	1.2 (0.21)	38.3 (2.10)	3.4 (0.46)
	70/30	1.3 (0.22)	37.5 (3.24)	2.9 (0.39)
PHBV/ESO	**95/5**	2.4 (0.10)	35.4 (0.29)	6.5 (0.14)
	90/10	2.1 (0.27)	31.2 (2.06)	6.9 (0.53)
	80/20	1.7 (0.30)	26.7 (3.63)	7.2 (0.96)
	70/30	0.8 (0.14)	20.7 (2.45)	7.5 (0.88)

[a] Number in the parenthesis is the standard deviation of the measurements.

The strength and modulus of PHBV/SO blends decreased and elongation at break also decreased as SO content in blends. However, when PHBV was blended with ESO, elongation at break was slightly improved. It would be concluded that ESO is more effective than SO as plasticizer of PHBV. This could be also verified from the notched Izod impact test results of PHBV blends. Figure 2 shows the variation of the impact strength of PHBV/SO and PHBV/ESO blend films with additive content. For the case of PHBV/SO blends the impact strength almost decreased gradually with the addition of SO. On the other hand, the impact strength of PHBV/ESO blends at 10% ESO content was more than twice that of PHBV, and thereafter slightly increased up to 30% ESO content.

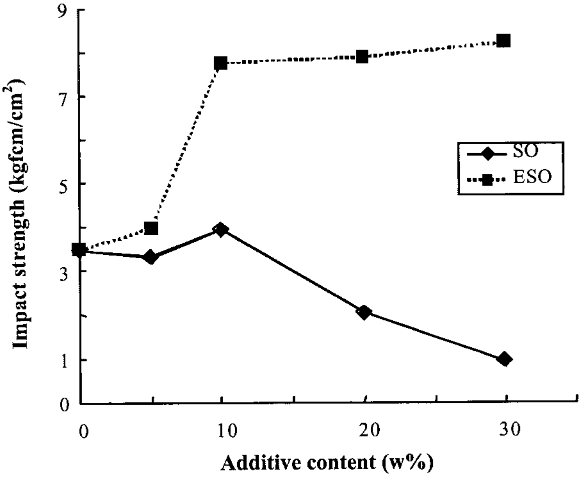


Figure 2. Impact Strength of PHBV blends as a function of additive content.

Figure 3 and 4 show the scanning electron micrographs of the etched fracture surfaces of PHBV/SO and PHBV/ESO blends, respectively. As seen in figures, the ESO domain size in the blends was smaller and more uniform than in PHBV/SO blends. This observation suggests that SO was less compatible with PHBV than ESO, and accordingly the segregation of SO in the blends occurred. Therefore, the improved ductility in PHBV/ESO blends could be attributed to its compatibility with PHBV.

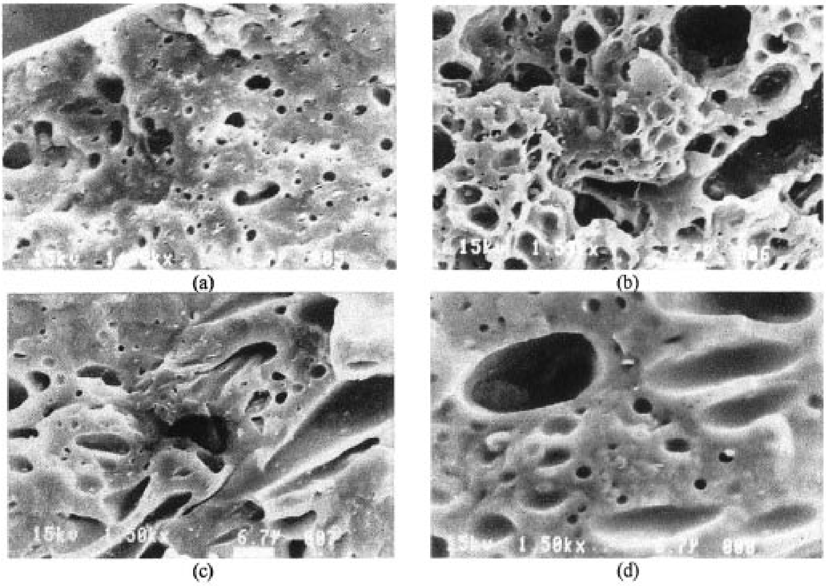
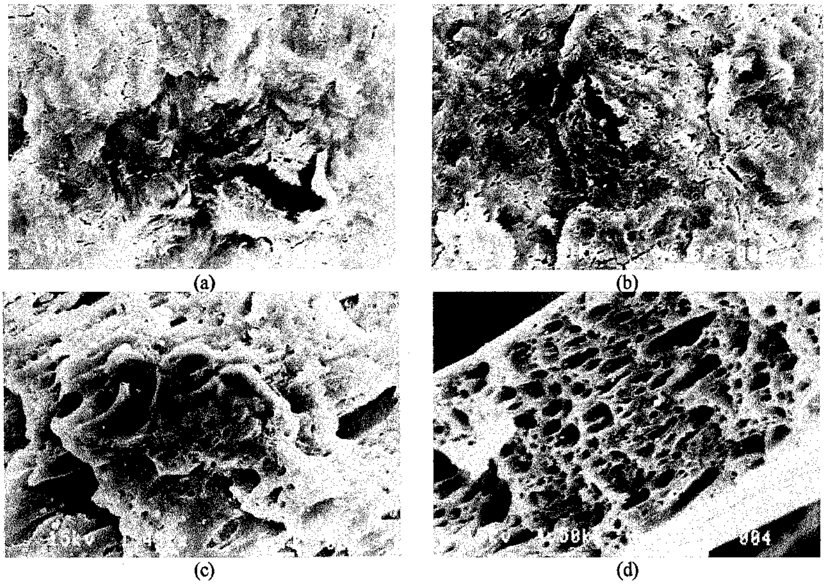


Figure 3. Scanning electron micrographs of fracture surfaces of PHBV/SO blend films: (a) PHBV/SO (95/5), (b) PHBV/SO (90/10), (c) PHBV/SO (80/20), (d) PHBV/SO (70/30).



(a) (b)

(c) (d)

Figure 4. Scanning electron micrographs of fracture surfaces of PHBV/ESO blend films: (a) PHBV/ESO (95/5), (b) PHBV/ESO (90/10), (c) PHBV/ESO (80/20), (d) PHBV/ESO (70/30).

Biodegradability of PHBV/additive Blends

In Figure 5 the biodegradation rate of PHBV/SO and PHBV/ESO blends is compared with that of PHBV. The additive content in the blends was 20 wt%. The addition of soybean oils (SO or ESO) dramatically accelerated the biodegradation as measured by weight loss during composting. The reason on accelerating effect of soybean oils to the biodegradation of PHBV was not clear because the biodegradation of polymers depends on several factors such as mobility of polymers, crystallinity and crystalline size and so on. However, it should be considered that soybean oils are not water-soluble and their biodegradation rate is known to be very fast in culture media and in field test.17,18) Therefore, we assumed that the accelerated biodegradation of PHBV blends in the early days was associated with the biodegradation of soybean oils. However, the noticeable difference in biodegradation rate between SO and ESO blends was not found until 20 days.

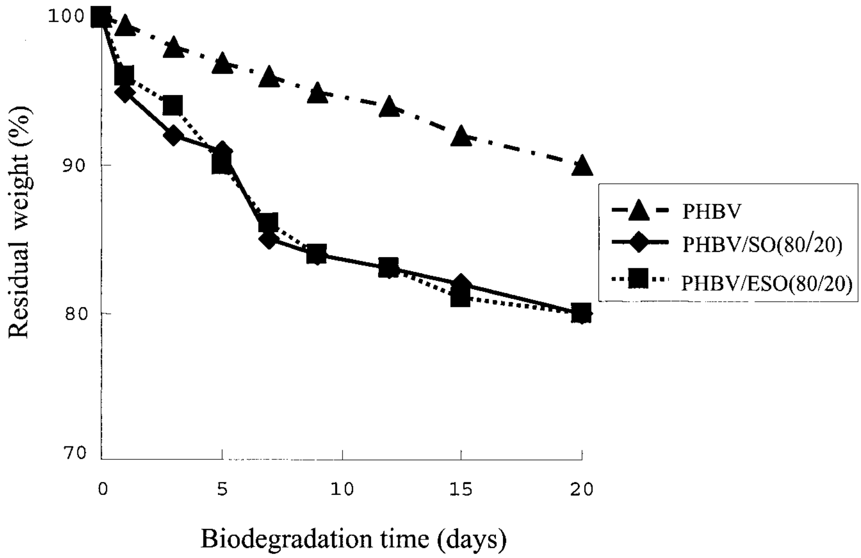


Figure 5. Biodegradation of PHBV and its blend films with 20% soybean oils.

Thermal Degradation of PHBV/Additive Blends

In order to investigate the thermal reactions in PHBV/additive blends, thermal degradation behavior of blends was conducted using dynamic TGA. Figure 6 shows the TGA thermograms of PHBV/SO (a) and PHBV/ESO (b) blends. The thermal degradation of pure PHBV proceeds by a one-step process with a maximum decomposition temperature. However, the thermal decomposition patterns of blends contained two separated degradation steps. As the additive content in blends increased, the second decomposition step increased in size without positional change (T_{max2} = 397±8°C for PHBV/SO blends, T_{max2} = 401±3°C for PHBV/ESO blends).

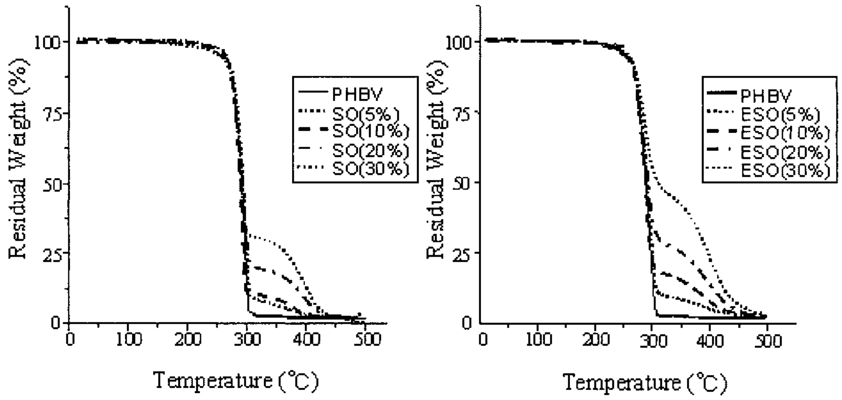


Figure 6. TGA thermograms of PHBV/additive blends: (a) PHBV/SO blends, (b) PHBV/ESO blends.

Figure 7 compares the residual weights at 350°C of PHBV/SO (a) and PHBV/ESO (b) blends. The dotted line corresponds to the residual weight of blends calculated on the basis of an additive rule with no interaction between the two components during the thermal degradation.

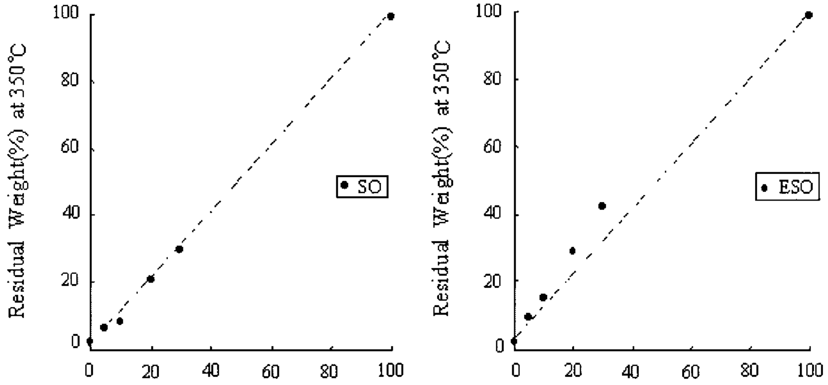


Figure 7. Effect of additive content (wt%) in PHB/additive blends on the residual weight at 350°C.

The residual weights of PHBV/ESO at 350°C had higher values than the ones calculated by additive rule and also the difference of their residual weights was higher as the ESO content increased from 0 to 30%, whereas the residual weights of PHBV/SO blends had the same values as the calculated ones. This supports the idea that the thermal reaction of the epoxide groups of ESO with carboxylic acid groups, which are formed by the random chain scission of PHBV component, occurred during the degradation of PHBV/ESO blends as shown in Figure 8. Reactions of this type during the thermal degradation of polymers have also been reported previously for PHB and its blends.[14,15,19]

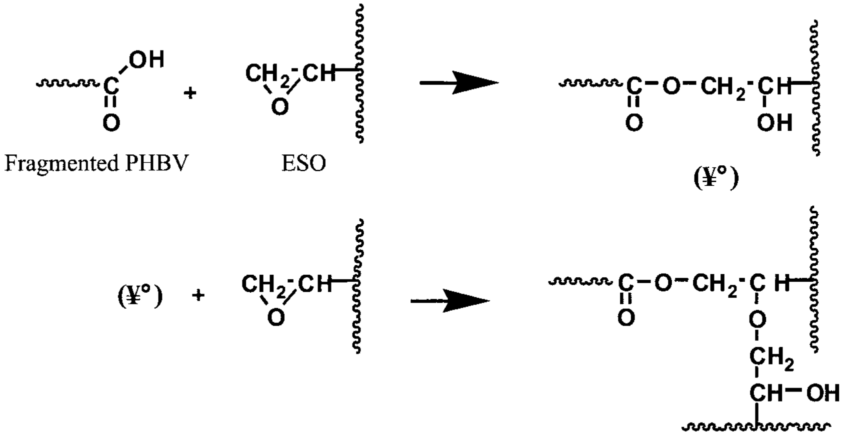


Figure 8. Thermal reactions between the fragmented PHBV and ESO during the thermal degradation process.

Acknowledgments

This work was supported by Korea Research Foundation Grant (KRF-2000-041-E00432).

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