

# Processability Modifications of Poly(3-hydroxybutyrate) by Plasticizing, Blending, and Stabilizing

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**ABSTRACT:** Poly(3-hydroxybutyrate) (PHB) was plasticized with dioctyl (*o*-)phthalate, dioctyl sebacate, and acetyl tributyl citrate (ATBC). The thermal properties, mechanical properties, and melt flow ability were studied with differential scanning calorimetry, thermogravimetric analysis, a universal material testing machine, and a melt flow indexer. ATBC was revealed to be an efficient plasticizer, reducing the glass-transition temperature and increasing the thermoplasticization ability of PHB. We also blended poly(3-hydroxybutyrate-*co*-hydroxyhexanoate) (PHBHHx) and poly(3-hydroxybutyrate-*co*-4-hydroxybuty-

rate) [P(3/4HB)] with PHB, ATBC, and antioxidant 1010 to overcome the brittleness of PHB and improve the melt flow stability of the materials. PHBHHx did little to improve the thermal processing but increased the fluidity of PHB, and P(3/4HB) toned the toughness of PHB. The addition of antioxidant 1010 enhanced the thermal stabilization of PHB. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 166–173, 2008

**Key words:** antioxidants; glass transition; processing; stabilization; thermal properties

## INTRODUCTION

Renewable and bacterially synthesized, poly(3-hydroxybutyrate) (PHB) is a completely biodegradable, highly hydrophobic thermoplastic polyester material containing a crystalline fraction of almost 80%.<sup>1,2</sup> The chemical structure and physical properties of PHB are fairly similar to those of certain petroleum-based synthetic polymers.<sup>3</sup> Therefore, PHB has been the subject of extensive studies as an environmentally friendly polymeric material. Because of its high crystallinity, PHB is stiff and brittle, and this results in very poor mechanical properties with a low extension at break, which limits its range of applications.<sup>4</sup> Until now, there has been no large commercial production of PHB products because of its higher cost with respect to commercial polymers, high brittleness, and difficult processing.

To reduce the excess brittleness and improve the overall physical properties of PHB and to obtain some useful new materials based on PHB, three kinds of methods have been extensively studied.<sup>5,6</sup> One is the bacterial synthesis of copolyesters containing hydroxyalkanoate units other than 3-hydrox-

ybutyrate. For example, PHB copolyesters containing 3-hydroxyvalerate<sup>7,8</sup> or 4-hydroxybutyrate<sup>9</sup> can be produced by *Alcaligenes eutrophus*. The composition of monomer units in these copolymers can be controlled with a mixture of different carbon sources in a culture medium. Through changes in the chemical and compositional structures of these copolyesters, their physical properties such as the melting point and crystallinity can vary widely.

The second way is to prepare PHB-based blends with other polymers or plasticizers.<sup>10</sup> Poly(ethylene oxide),<sup>11,12</sup> poly(vinyl alcohol),<sup>13</sup> synthetic atactic PHB,<sup>14,15</sup> polysaccharides,<sup>16</sup> poly( $\epsilon$ -caprolactone),<sup>17,18</sup> poly(vinyl phenol),<sup>19,20</sup> poly(vinyl acetate),<sup>21–23</sup> poly(lactic acid),<sup>24</sup> xylogen,<sup>25</sup> and even dendritic polyester oligomers<sup>26</sup> have been used for this purpose. Blending PHB with high- or low-molecular-weight components can provide a relatively inexpensive and simple route for improving some physical properties and reducing the production cost of plastic articles. The third way is the synthesis of PHB copolymers through copolymerization with other monomers. Several block copolymers have been synthesized and used as compatibilizers for polymer blending to improve the mechanical properties.<sup>6,27–30</sup>

In the investigations of PHB plasticizers up to now, the studied plasticizers have not seemed very effective. We therefore tried to use a combination of plasticizers with some amorphous polyhydroxyalkanoates such as poly(3-hydroxybutyrate-*co*-hydroxyhexanoate) (PHBHHx) and poly(3-hydroxybutyrate-

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co-4-hydroxybutyrate) [P(3/4HB)] and even antioxidants to modify the processability and widen the processing window of PHB.

## EXPERIMENTAL

### Materials

PHB [number-average molecular weight ( $M_n$ ) =  $3.3 \times 10^5$ , weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ ) = 2.5, as estimated by gel permeation chromatography; Jiangsu NanTian, Nantong, China], PHBHHx ( $M_n = 4.0 \times 10^4$ ,  $M_w/M_n = 1.9$ ; homemade) with 12 wt % hydroxyhexanoate, P(3/4HB) ( $M_n = 4.4 \times 10^5$ ,  $M_w/M_n = 1.8$ ; Tianjin GreenBio, Tianjin, China) with 36 wt % 4HB (calculated from  $^1\text{H-NMR}$ ), plasticizers, and other reagent-grade chemicals were used as received without further purification.

### Preparation of the blend films

The PHB blend films were prepared through the dissolution of 3 g of PHB and other components in 100 mL of chloroform, refluxing for 1 h, cooling, and casting onto a glass dish. After the evaporation of chloroform, the resultant films were dried *in vacuo* for 2 days to a constant weight.

### Characterization of the PHB-based blends

#### Differential scanning calorimetry (DSC) analysis

The thermal transitions of the blends were characterized by DSC performed on a TA Instruments (New Castle, DE) Q100 with an autocool accessory and calibrated with indium over a temperature range of  $-80$  to  $180^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere ( $50 \text{ mL}/\text{min}$ ). After being kept at  $180^\circ\text{C}$  for 1 min, the molten sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ . Subsequently, the sample was again heated from  $-80$  to  $180^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The second heating round of the DSC curves was used to analyze the thermal properties. The glass-transition temperature ( $T_g$ ) was taken as the midpoint of the heat capacity change. The melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_f$ ) were determined from endothermic DSC peaks. In the presence of multiple endothermic peaks, the maximum peak temperature was taken to be  $T_m$ . The cold-crystallization temperature ( $T_c$ ) and cold-crystallization enthalpy ( $\Delta H_c$ ) were determined from the corresponding exothermic DSC peaks.

#### Thermogravimetric analysis (TGA)

TGA was performed on a Q-50 instrument (TA Instruments, New Castle, DE) calibrated with indium. The

temperature was ramped at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen to a temperature well above the degradation temperature of the polymers ( $450^\circ\text{C}$ ).

### Mechanistic test

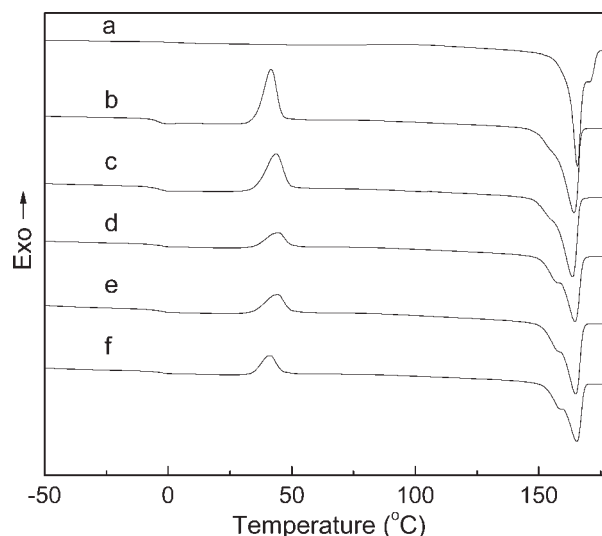
Dumbbell-shaped samples of PHB-based films (thickness =  $0.3\text{--}0.4 \text{ mm}$ , base width =  $6 \text{ mm}$ , base length =  $10 \text{ cm}$ ) were used for mechanical tests. The elongation at break, tensile strength, and Young's modulus of the tested samples was determined with a CMT 4204 universal testing machine (Sans, Shenzhen, China) at room temperature with an extension rate of  $5 \text{ mm}/\text{min}$ . The values are the average values of five determinations.

### Melt flow index (MFI) measurement

Five grams of PHB-based blends was used for MFI measurements with a ZRZ1402 melt flow indexer (Sans) at  $160^\circ\text{C}$  with a weight of  $2160 \text{ g}$ . Because of the thermal instability of PHB, the lower test temperature of  $160^\circ\text{C}$  was used.

## RESULTS AND DISCUSSION

At the beginning of the study, a blend of PHB with the most common plasticizer, dioctyl (*o*-)phthalate (DOP), was tested. DOP did have some plasticizing effect on PHB, such as a  $T_g$  value as low as  $-9^\circ\text{C}$  and an elongation at break as low as 13% with 30% DOP. Because of concerns about the toxic uncertainty of the plasticizer, we selected some nontoxic plasticizers such as dioctyl sebacate (DOS) and acetyl tributyl citrate (ATBC) for our investigation.



**Figure 1** DSC thermograms of (a) pure PHB, (b) a PHB/25 wt % DOS blend, (c) a PHB/30 wt % DOS blend, (d) a PHB/35 wt % DOS blend, (e) a PHB/40 wt % DOS, and (f) a PHB/50 wt % DOS blend.

**TABLE I**  
Thermal Properties of Pure PHB and PHB/DOS Blends  
Obtained from the Second-Heating-Round Thermograms

DOS (wt %)	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_f$ (J/g)
0	6.1	—	—	169.0	82.1
25	-4.2	41.8	35.0	164.2	70.3
30	-3.6	43.8	31.4	163.5	66.2
35	-2.8	44.5	13.9	164.6	54.6
40	-2.8	44.3	16.9	164.9	57.8
50	-2.4	41.4	14.6	165.4	48.5

A 2-mg sample was packed in an aluminum pan and then heated from  $-80$  to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (first run). After 1 min of annealing, the sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ , annealed for 1 min, and then reheated to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (second run).

### PHB/DOS blends

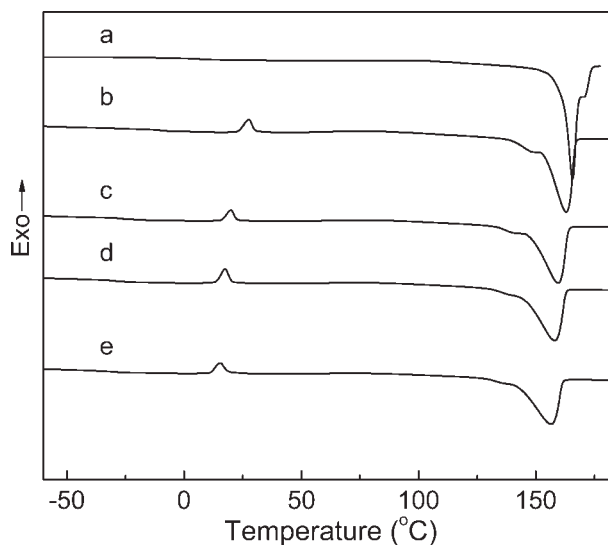
DSC thermograms of the pure PHB and PHB/DOS blends are shown in Figure 1. The data are listed in Table I and reveal that with an increase in the DOS content,  $T_g$ ,  $T_c$ , and  $T_m$  of the blends change little. However,  $\Delta H_f$  and  $\Delta H_c$  decrease obviously. This might mean that plasticizer DOS increases the crystallization rate of PHB but has a very limited effect on the amorphous region and the crystallization degree in the materials.

The elongation at break, tensile strength, and Young's modulus of PHB and PHB/DOS blends are shown in Table II. With an increase in the DOS content, the tensile strength and Young's modulus of the blends decrease, but the elongation at break shows no visible advance. Also, when the DOS content is about 35 wt %, the blend shows the best mechanical properties. Compared with DOP, DOS has less of a plasticizing effect on PHB. It is generally recognized that DOS is a kind of plasticizer that can enter only the amorphous region and not enter the crystalline region. The plasticizing effect is thus not so strong, and DOS is usually used as the secondary plasticizer only. In our study, we also

**TABLE II**  
Mechanical Properties of PHB/DOS Blends

DOS (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
0	$14.0 \pm 1.2$	$2.5 \pm 0.5$	$1510.4 \pm 65.8$
25	$7.5 \pm 0.4$	$3.9 \pm 0.3$	$592.7 \pm 45.8$
30	$6.3 \pm 0.4$	$4.3 \pm 0.6$	$374.1 \pm 67.7$
35	$5.1 \pm 0.3$	$5.4 \pm 0.9$	$458.9 \pm 38.5$
40	$4.5 \pm 0.5$	$5.2 \pm 0.6$	$402.8 \pm 48.6$

Dumbbell-shaped samples of PHB-based films (thickness =  $0.3\text{--}0.4$  mm, base width = 6 mm, base length = 10 cm) were used for mechanical tests at room temperature with a pulling rate of 5 mm/min. The values are the average values of five determinations.



**Figure 2** DSC thermograms of (a) pure PHB, (b) a PHB/10 wt % ATBC blend, (c) a PHB/20 wt % ATBC blend, (d) a PHB/25 wt % ATBC blend, and (e) a PHB/30 wt % ATBC blend.

observed the plasticizer leak out from the surface when the DOS concentration was more than 30%.

### PHB/ATBC blends

The DSC thermograms of the pure PHB and PHB/ATBC blends are shown in Figure 2, and the thermal data are given in Table III. The striking feature is that  $T_g$  of PHB decreases sharply with the content of ATBC. The DSC results also show that  $T_m$  and  $\Delta H_f$  of the blends decrease with an increasing amount of ATBC in comparison with the pure PHB. A similar result was reported by Baiardo et al.,<sup>31</sup> who analyzed PLA/ATBC blends over a composition range (0–45% ATBC). With an increase in the ATBC content, the blends possess much lower  $T_g$ ,  $T_m$ , and  $\Delta H_f$  values. This indicates that ATBC exhibits a much better plasticizing effect for PHB than previously dis-

**TABLE III**  
Thermal Properties of Pure PHB and PHB/ATBC Blends  
Obtained from the Second-Heating-Round Thermograms

ATBC (wt %)	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_f$ (J/g)
0	6.1	—	—	169.0	82.1
10	-9.8	27.6	5.9	162.9	80.2
20	-28.5	20.0	4.5	159.6	67.4
25	-29.7	17.6	6.5	158.3	65.9
30	-30.7	15.5	5.5	156.8	60.6

A 2-mg sample was packed in an aluminum pan and then heated from  $-80$  to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (first run). After 1 min of annealing, the sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ , annealed for 1 min, and then reheated to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (second run).

**TABLE IV**  
Mechanical Properties of PHB/ATBC Blends

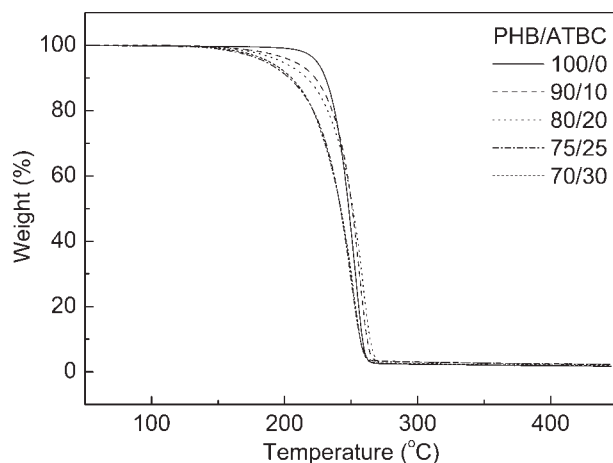
ATBC (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
0	14.0 ± 1.2	2.5 ± 0.5	1510.4 ± 65.8
10	14.3 ± 1.1	6.1 ± 0.8	1366.7 ± 74.6
20	10.2 ± 0.5	8.5 ± 0.9	685.0 ± 47.4
25	9.5 ± 0.8	8.8 ± 0.7	476.4 ± 43.9
30	6.1 ± 0.6	9.7 ± 0.7	192.7 ± 39.5

Dumbbell-shaped samples of PHB-based films (thickness = 0.3–0.4 mm, base width = 6 mm, base length = 10 cm) were used for mechanical tests at room temperature with a pulling rate of 5 mm/min. The values are the average values of five determinations

cussed DOS. As the more polar and low-molecular-weight plasticizer, ATBC may insert between the polymer chains and enlarge the distance between the polymers and may also reduce the viscosity of the polymers. This produces the profound plasticizing effect.

A mechanical analysis of the PHB/ATBC blend system is presented in Table IV. With an increase in ATBC to 30 wt %, the elongation at break increases from 2.5 to 9.7%. However, the tensile strength decreases from 14.3 to 6.1 MPa, and Young's modulus decreases from 1510.4 to 192.7 MPa. This means that the mechanical properties of PHB cannot be greatly improved by plasticizer ATBC. The reason might be that the plasticizing effect is mainly limited to the amorphous region, which accounts for only a small portion in PHB materials. It is also understood that the plasticizers reduce the rigidity and increase the ductility, and the modulus and tensile strength decrease accordingly.

The TGA curves of pure PHB and ATBC-plasticized PHB, shown in Figure 3, were obtained from room temperature to 450°C at a heating rate of



**Figure 3** TGA curves of pure PHB and PHB/ATBC blends.

**TABLE V**  
TGA Parameters of Pure PHB and PHB/ATBC Blends

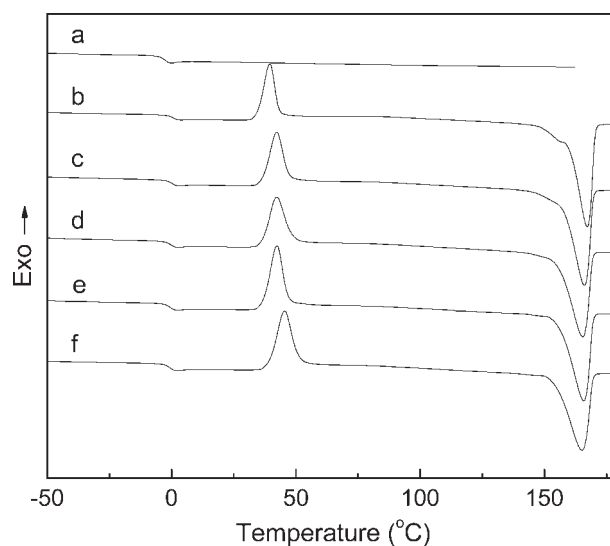
ATBC (%)	0	10	20	25	30
$T_{d(5\%)} (^{\circ}\text{C})^a$	224.2	208.2	195.1	185.9	188.7

<sup>a</sup> Temperature at 5% weight loss determined by TGA.

10°C/min. With an increase in the ATBC content, the initial weight loss temperature decreases slightly. The temperature at a 5% weight loss of the blends changes from 224.2 to 188.7°C (Table V) when the ATBC content increases up to 30%. However, the maximal degradation temperatures remain close to one another. The addition of ATBC lowers the initial degradation temperatures but not the bulk degradation temperature. This might be caused by some lower boiling point impurities in the ATBC plasticizer.

#### PHB/PHBHHx blends

As discussed previously, the addition of plasticizer ATBC leads to a noticeable decrease in  $T_g$  and improvements in the other thermal characteristics. However, the mechanical properties change very little. The reason might be the limited amorphous portion in the materials. Therefore, low-molecular-weight PHBHHx ( $M_n = 75,000$ ), which is a completely amorphous and soft material with a  $T_g$  value of  $-3^{\circ}\text{C}$ , was blended with PHB with the intention of increasing the amorphous region and improving the PHB brittleness. The second heating thermograms of the pure PHBHHx and PHB/PHBHHx



**Figure 4** DSC thermograms of (a) pure PHBHHx, (b) a PHB/5 wt % PHBHHx blend, (c) a PHB/10 wt % PHBHHx blend, (d) a PHB/15 wt % PHBHHx blend, (e) a PHB/20 wt % PHBHHx blend, and (f) a PHB/25 wt % PHBHHx blend.



**TABLE VI**  
**Thermal Properties of Pure PHB, PHBHHx, and PHB/PHBHHx Blends Obtained from the Second-Heating-Round Thermograms**

PHBHHx (wt %)	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_f$ (J/g)
0	6.1	—	—	169.0	82.1
5	0.4	39.5	30.4	167.2	82.9
10	0.0	42.4	34.4	166.1	81.2
15	-0.1	42.4	38.1	165.5	76.2
20	-0.3	42.3	39.1	165.8	75.3
25	-0.3	45.4	42.6	165.2	72.3
100	-3.0	—	—	—	—

Two-milligram samples were packed in an aluminum pan and then heated from  $-80$  to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (first run). After 1 min of annealing, each sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ , annealed for 1 min, and then reheated to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (second run).

blends are given in Figure 4. Detailed information is presented in Table VI. The thermal properties change little in the samples. PHBHHx alone cannot improve the thermal properties of PHB. The reason might be the very close  $T_g$  values of PHBHHx and PHB, which are  $-3.0$  and  $6.1^\circ\text{C}$ , respectively. Because of its close  $T_g$ , PHBHHx cannot effectively plasticize the PHB materials to lower their  $T_g$  values. A mechanical analysis of the PHB/PHBHHx blend system is presented in Table VII. With an increase in PHBHHx to 20 wt %, the elongation at break increases from 1.6 to 4.5%, the tensile strength increases from 15.3 to 16.7 MPa, and Young's modulus decreases from 1604.4 to 1137.0 MPa. This means that the mechanical properties of PHB can be improved by PHBHHx with limited extension.

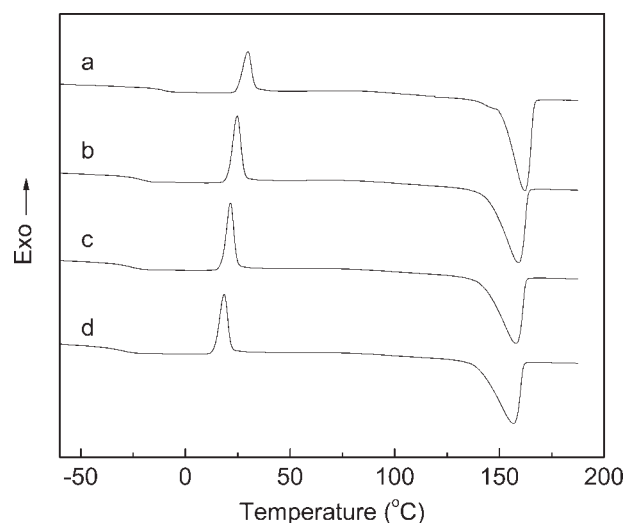
#### PHB/PHBHHx/ATBC blends

To further improve the processability of PHB, both PHBHHx and plasticizer ATBC were used for the modifications of PHB materials. The DSC thermo-

**TABLE VII**  
**Mechanical Properties of PHB/PHBHHx Blends**

PHBHHx (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
0	$14.0 \pm 1.2$	$2.5 \pm 0.5$	$1510.4 \pm 65.8$
5	$15.3 \pm 0.3$	$1.6 \pm 0.9$	$1604.4 \pm 87.6$
10	$16.6 \pm 0.5$	$4.1 \pm 0.8$	$1480.5 \pm 72.5$
15	$16.7 \pm 0.6$	$3.5 \pm 1.0$	$1403.9 \pm 90.6$
20	$15.7 \pm 0.7$	$4.5 \pm 0.4$	$1137.0 \pm 53.0$

Dumbbell-shaped samples of PHB-based films (thickness =  $0.3$ – $0.4$  mm, base width = 6 mm, base length = 10 cm) were used for mechanical tests at room temperature with a pulling rate of  $5$  mm/min. The values are the mean values of five determinations.



**Figure 5** DSC thermograms of (a) a PHB/PHBHHx/10 wt % ATBC blend, (b) a PHB/PHBHHx/20 wt % ATBC blend, (c) a PHB/PHBHHx/25 wt % ATBC blend, and (d) a PHB/PHBHHx/30 wt % ATBC blend (in all these tests, 10 wt % PHBHHx with respect to the total weight was used).

grams are shown in Figure 5. The thermal and mechanical property data of the blends are summarized in Tables VIII and IX, respectively. Comparing Tables III and VIII, we find that PHBHHx has little effect on the thermal behavior of the PHB/PHBHHx/ATBC system. The combination of PHBHHx and ATBC, however, has a synergetic effect on improving the properties of PHB. With a content ratio of 10% PHBHHx to 30% ATBC, the PHB blend materials show a lowering of  $T_g$  (from  $6.1^\circ\text{C}$  for neat PHB to  $-30.6^\circ\text{C}$ ) and increases in the elongation at break (from 2.5 to 15.7%) and Young's modulus (from 568.6 to 696.0 MPa) at the cost of a very low loss of the tensile strength (from 9.9 to 7.7 MPa). This result reveals that the PHB/PHBHHx/ATBC blend is a quite good system for modifying the properties of PHB.

**TABLE VIII**  
**Thermal Properties of PHB/PHBHHx/ATBC Blends Obtained from the Second-Heating-Round Thermograms**

ATBC (wt %)	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_f$ (J/g)
10	-10.1	29.9	15.6	162.2	67.9
20	-20.8	24.8	23.6	159.0	67.7
25	-26.3	21.5	22.1	157.9	62.8
30	-30.6	18.5	20.6	156.7	59.1

The weight ratio of PHBHHx was 10 wt % with respect to the total weight. Two-milligram samples were packed in an aluminum pan and then heated from  $-80$  to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (first run). After 1 min of annealing, each sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ , annealed for 1 min, and then reheated to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (second run).

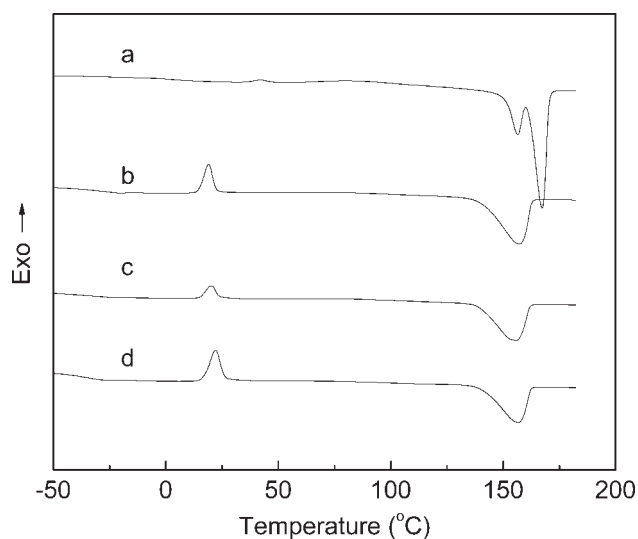
**TABLE IX**  
Mechanical Properties of PHB/PHBHHx/ATBC Blends

ATBC (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
10	9.9 ± 1.0	2.1 ± 0.4	568.6 ± 54.0
20	10.7 ± 0.2	8.6 ± 0.6	792.3 ± 46.0
25	8.1 ± 0.9	9.1 ± 1.3	521.3 ± 84.9
30	7.7 ± 0.3	15.7 ± 0.6	696.0 ± 95.2

The weight ratio of PHBHHx was 10 wt % with respect to the total weight. Dumbbell-shaped samples of PHB-based films (thickness = 0.3–0.4 mm, base width = 6 mm, base length = 10 cm) were used for mechanical tests at room temperature with a pulling rate of 5 mm/min. The values are the mean values of five determinations.

### PHB/P(3/4HB)/ATBC blends

At last, P(3/4HB), a completely amorphous material with a  $T_g$  value of  $-19^\circ\text{C}$ , was blended with PHB to improve the mechanical properties. The DSC thermograms and mechanical property data are shown in Figure 6 and Tables X and XI, respectively. The PHB/P(3/4HB)/ATBC blends show even lower  $T_g$  values up to  $-35.7^\circ\text{C}$  in comparison with those of the PHB/ATBC blends. The elongation at break of the PHB/P(3/4HB)/ATBC blend is much larger than that of the PHB/ATBC system, up to 35.2% from 9.2%. However, the tensile strength and Young's modulus decrease to very low levels, with values of 1.0 and 18.3 MPa when 30% PHB and 30% ATBC are added, respectively. The low tensile strength and Young's modulus might be caused by the poor miscibility of the blends, which is still under investigation. These results also suggest that a combination of



**Figure 6** DSC thermograms of (a) pure PHB/ATBC, (b) a PHB/ATBC/10 wt % P(3/4HB) blend, (c) a PHB/ATBC/20 wt % P(3/4HB) blend, and (d) a PHB/ATBC/30 wt % P(3/4HB) blend (in all these tests, 30 wt % ATBC with respect to the total weight was used).

**TABLE X**  
Thermal Properties of PHB/P(3/4HB)/ATBC Blends Obtained from the Second-Heating-Round Thermograms

P(3/4HB) (wt %)	$T_g$ ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )	$\Delta H_c$ (J/g)	$T_m$ ( $^\circ\text{C}$ )	$\Delta H_f$ (J/g)
0	-30.7	15.5	5.5	156.8	60.6
10	-24.3	19.0	11.8	157.0	53.3
20	-26.4	20.4	6.2	155.8	43.3
30	-35.7	22.1	16.1	156.3	40.5

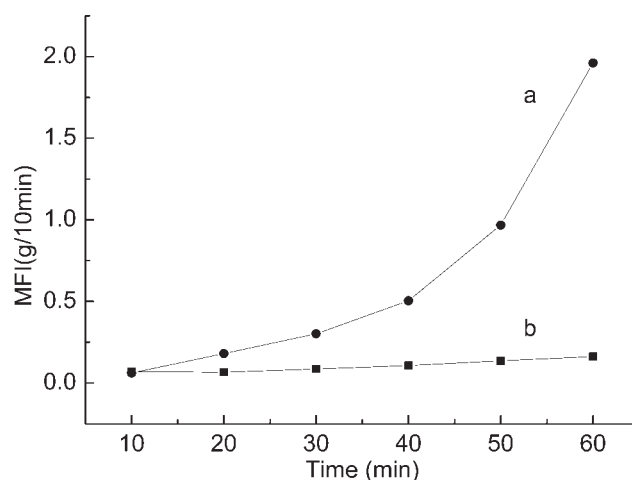
The weight ratio of ATBC was 30 wt % with respect to the total weight. Two-milligram samples were packed in an aluminum pan and then heated from  $-80$  to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (first run). After 1 min of annealing, the sample was quenched to  $-80^\circ\text{C}$  at a cooling rate of  $80^\circ\text{C}/\text{min}$ , annealed for 1 min, and then reheated to  $180^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  (second run).

**TABLE XI**  
Mechanical Properties of PHB/ATBC Blends and PHB/P(3/4HB)/ATBC Blends

P(3/4HB) (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
0	6.1 ± 0.6	9.7 ± 0.7	192.7 ± 39.5
10	2.8 ± 0.5	17.0 ± 0.7	118.3 ± 15.2
20	2.0 ± 0.2	24.0 ± 1.1	66.4 ± 17.5
30	1.0 ± 0.1	35.2 ± 0.9	18.3 ± 6.7

The weight ratio of ATBC was 30 wt % with respect to the total weight. Dumbbell-shaped samples of PHB-based films (thickness = 0.3–0.4 mm, base width = 6 mm, base length = 10 cm) were used for mechanical tests at room temperature with a pulling rate of 5 mm/min. The values are the mean values of five determinations.

P(3/4HB) and plasticizer ATBC would modify PHB into a soft, ductile, and weak material, which may find some applications in biomedicine, such as cell culture scaffolds.



**Figure 7** MFI versus the time for (a) a PHB/ATBC (70/30) blend and (b) a PHB/ATBC/antioxidant 1010 (70/30/5) blend.

TABLE XII  
MFIs (g/10 min) of PHB-Based Blends

Time (min)	10	20	30	40	50	60
PHB/ATBC	0.0612	0.1805	0.3016	0.5038	0.9679	1.9610
PHB/ATBC/1010	0.0694	0.0657	0.0853	0.1065	0.1361	0.1617
PHB/ATBC/PHBHHx	0.3962	0.4490	0.5003	0.5050	0.6041	—
PHB/ATBC/PHBHHx/1010	0.3899	0.4152	0.4248	0.4582	0.4785	—
PHB/ATBC/P(3/4HB)	0.0302	0.0456	0.0605	0.1235	0.2027	0.2352
PHB/ATBC/P(3/4HB)/1010	0.0250	0.0351	0.0465	0.0585	0.0842	0.1204

The conditions were 160°C and 2160 g. The weight ratio of antioxidant 1010 was 5 wt %, the weight ratio of ATBC was 30 wt %, the weight ratio of PHBHHx was 10 wt %, and the weight ratio of P(3/4HB) was 10 wt % with respect to the total weight.

### Effect of a stabilizing agent on PHB

The thermal stability of PHB is quite poor, and thermal degradation is usually encountered during thermal processing such as extrusion and injection. The MFI or melt flow rate increased sharply in the melt flow indexer with time during our MFI measurements. To improve the processing stability, PHB was studied by the addition of antioxidant 1010. The MFI measurement conditions were 160°C and 2160 g. We chose the lower temperature to keep the degradation of PHB as low as possible. The MFI curves of ATBC-plasticized PHB are shown in Figure 7. Antioxidant 1010, a kind of stabilizer widely used in commodity polymers, was tested for the stabilization of polyhydroxylalkanoates. All the MFI data are summarized in Table XII. In the PHB/ATBC system, the addition of antioxidant 1010 improves the PHB thermal stability greatly. Without the addition of antioxidant 1010, the MFI of PHB increases rapidly [Fig. 7(a)]. With the addition of antioxidant 1010, the MFI value, however, shows little change during the measurement period [Fig. 7(b)]. In the PHB/PHBHHx/ATBC and PHB/P(3/4HB)/ATBC systems, it displays similar improvements in the thermal stability. Comparing the MFI changes without antioxidant 1010, we find that the addition of PHBHHx and P(3/4HB) can also enhance the thermal stability of PHB to some extent. This might be due to the high melt viscosity of the amorphous materials, which possess a lower thermal degradation rate during melting. Antioxidant 1010, a kind of hindered phenol, can prevent aging and degradation via its phenol-hydroxyl catch on the free radical. During MFI measurement and heat processing, the degradation of PHA is caused, and a free radical is formed during the process.<sup>32</sup> This radical further propagates, and further degradation occurs if the radical is not quenched immediately. Antioxidant 1010, however, quenches the radical and stops further degradation. This is why the MFI value can be stabilized and the thermal degradation can be inhibited.

### CONCLUSIONS

Poly(3-hydrobutyrate) has been plasticized with DOP, DOS, and ATBC. From the DSC measurements, it can be concluded that only the addition of ATBC leads to an obvious decline in  $T_g$  and improves other thermal characteristics. However, it does little to improve the mechanical properties. Blending with P(3/4HB) improves the mechanical properties of PHB obviously, with a good elongation at break obtained. The MFI test has revealed that the addition of stabilizer antioxidant 1010 and the addition of PHBHHx and P(3/4HB) enhance the thermal stability of PHB and stabilize the MFI value. A combination of ATBC, antioxidant 1010, and PHBHHx or P(3/4HB) could widen the PHB processing window.

### References

- Hoffmann, A.; Kreuzberger, S.; Hinrichsen, G. *Polym Bull* 1994, 33, 355.
- Ivica, J.; Igor, L.; Ivan, C. *Polym Degrad Stab* 2002, 77, 35.
- Tsuyoshi, F.; Harumi, S.; Rumi, M.; Zhang, J. M.; Duan, Y. X.; Isao, N.; Shukichi, O.; Yukihiko, O. *Macromolecules* 2005, 38, 6445.
- Savenkova, L.; Gercberga, Z.; Nikolaeva, V.; Dzene, A.; Bibers, I.; Kalnin, M. *Process Biochem* 2000, 35, 5739.
- Xing, P. X.; Ai, X.; Dong, L. S.; Feng, Z. L. *Macromolecules* 1998, 31, 6898.
- Giuseppe, I.; Mario, G.; Tony, B.; Giuseppe, M.; Alberto, B. *Biomacromolecules* 2002, 3, 835.
- Doi, Y. *Microbial Polyesters*; VCH: New York, 1990.
- Holmes, P. A. *Phys Technol* 1985, 16, 32.
- Kunioka, M.; Kawaguchi, Y.; Doi, Y. *Appl Microbiol Biotechnol* 1987, 30, 569.
- Rodrigo, C. B.; Lucia, H.; Innocentini, M.; Julio, B. *Macromol Symp* 2003, 197, 33.
- Avella, M.; Martuscelli, E. *Polymer* 1988, 29, 1731.
- Avella, M.; Greco, P.; Martuscelli, E. *Polymer* 1991, 32, 1647.
- Azuma, Y.; Yoshie, N.; Sakurai, M.; Inoue, Y.; Chujo, R. *Polymer* 1992, 33, 4763.
- Pearce, R.; Marchessault, R. H. *Polymer* 1994, 35, 3990.
- Abe, H.; Doi, Y.; Satkowski, M. M.; Noda, I. *Macromolecules* 1994, 27, 50.
- Finelli, L.; Scandola, M. S.; Sadocco, P. *Macromol Chem Phys* 1998, 199, 695.

17. Dave, P. B.; Parikh, M.; Reeve, M.; Gross, R. A.; McCarthy, S. P. *Polym Mater Sci Eng* 1990, 63, 726.
18. Kumagai, Y.; Doi, Y. *Polym Degrad Stab* 1992, 36, 241.
19. Iriondo, P.; Iruin, J. J.; Fernandez-Berridi, M. J. *Polymer* 1995, 36, 3235.
20. Xing, P.; Dong, L.; An, Y.; Feng, Z.; Avella, M.; Martuscelli, E. *Macromolecules* 1997, 30, 2726.
21. Greco, P.; Martuscelli, E. *Polymer* 1989, 3, 1475.
22. An, Y. X.; Dong, L. S.; Li, L. X. *Eur Polym* 1999, 35, 365.
23. An, Y. X.; Dong, L. S.; Li, L. X. *J Polym Sci Part B: Polym Phys* 1999, 37, 443.
24. Ohkoshi, I.; Abe, H.; Doi, Y. *Polymer* 2000, 15, 5985.
25. Wei, H. K.; He, Y.; Asakava, N. *J Appl Polym Sci* 2004, 94, 2466.
26. Xu, S. L.; Luo, R. C.; Wu, L. P.; Xu, K. T.; Chen, G. Q. *J Appl Polym Sci* 2006, 102, 3782.
27. Fayt, R.; Jerome, R.; Teyssie, P. *Polym Eng Sci* 1987, 27, 328.
28. Fayt, R.; Jerome, R.; Teyssie, P. *Makromol Chem* 1986, 187, 837.
29. Heuschen, J.; Vion, J. M.; Jerome, R.; Teyssie, P. *Polymer* 1990, 31, 1473.
30. Hosoda, S.; Kihara, H.; Kojima, K.; Satoh, Y.; Doi, Y. *Polym J* 1991, 23, 277.
31. Massimo, B.; Giovanna, F.; Mariastella, S.; Michel, R.; David, L.; Kurt, R.; Erich, W. *J Appl Polym Sci* 2003, 90, 1731.
32. Roy, S. L.; Robert, J. W. *Macromolecules* 1994, 27, 3782.