Crystallization Behavior and Thermal Properties of Blends of Poly(3-hydroxybutyate-co-3-valerate) and Poly(1,2-propandiolcarbonate)

Long Chen,[1] *Meifang Zhu,**[1] *Liyuan Song,*[1] *Hao Yu,*[1]
Yu Zhang,[1] *Yanmo Chen,*[1] *H. J. Adler*[2]

[1] College of Material Science & Engineering, State Key Laboratory for Modification of Chemical Fiber & Polymeric Materials, Dong Hua University, Shanghai 200051, China
E-mail: zmf@dhu.edu.cn
[2] Institute of Macromolecular Chemistry & Textile Chemistry, Dresden University of Technology, Mommsenstr. 13, D-01069 Dresden, Germany

Summary: Crystallization behavior of blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(1,2-propandiolcarbonate) ($PR(CO_2)$) has been investigated by polarized light microscopy (PLM). The spherulite growth rates (SGR) of all blends were faster than that of pure PHBV, and the spherulite growth rates of PHBV in the PHBV/$PR(CO_2)$ blends reduced with increasing $PR(CO_2)$ weight fraction. There are two melting peaks in both the pure PHBV and the PHBV/$PR(CO_2)$ blends. The melting peak of PHBV/$PR(CO_2)$ blends was reduced by lower temperature about 20K as compared to PHBV and the higher temperature melting peak was increased by about 10K in the blends.
Keywords: blends; crystallization behavior; thermal properties

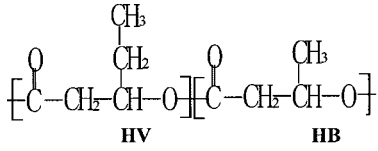
1. Introduction

Among environmentally friend polymeric materials, the bacterial organ poly(hydroxyalkanoate)s (PHAs) is a kind of high-molecular-weight polyesters produced by a wide range of microorganisms as intracellular carbon and energy reserve materials[1]. Poly(hydroxybutyrate) (PHB) are principal type of PHAs. PHB is relatively abundant in the environment and may be found in soil bacteria[2], estuarine micro-flora[3], blue-green algae[4] and micro-bially treated sewage[5]. The percentage of PHB in these cells is normally low, between 1 and 30%, but under controlled fermentation condition of corn

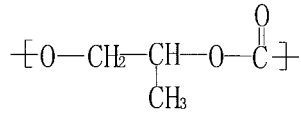
 DOI: 10.1002/masy.200450628

starch and nitrogen limitation and overproduction of PHB can be encouraged directly and yields increased to about 70% of dry cell weight[6]. In all cases the polymer occurs as discrete granules within the living organisms and may be extracted from them using a variety of organic solvents such as chloroform[7], ethylene dichloride[8], methylene chloride[9], pyridine[10] and propylene carbonate[11].

Recently PHAs have attracted much attention as an excellent biocompatible, bioabsorbable and biodegradable thermoplastic[12]. However, there are several shortcomings to commercial use of the PHB. Because it is produced from microorganisms, it is relatively expensive compared with other biodegradable polymers. Also it has a very narrow processing window due to their poor thermal stability[13] and it is rather brittle for use below the glass transition temperature (*Tg*). To reduce its brittle character, various copolymers that have different types of aliphatic polyester units, for example poly(hydroxybutyrate-*co*-hydroxyvalerate)(PHBV) presents over PHB homopolymer the advantages of improved thermostability and toughness[14-18].



Unit structure of PHBV



Unit structure of PR(CO_2)

Fig. 1. Chemical structures of PHBV and PR(CO_2).

Another approach to modify the properties of PHB and PHBV is to form polymer blends with synthetic or biodegradable polymers. Through blending with other polymers, the cost of the final materials can be reduced and the mechanical properties of PHB and PHBV can be improved. Many investigators have studied thermal behavior, crystallization, and mechanical properties of blends of the PHB and PHBV with synthetic and other biodegradable polymers such as poly(ethylene oxide)[19,20], poly(vinyl acetate)[21],

poly(vinyl alcohol)[22], cellulose ester[23], poly(ε-caprolactone)(PCL)[24], and poly(styrene-*co*-acrylonitrile)(SAN)[12]. In this paper, the effect of carbon dioxide copolymer resin ($PR(CO_2)$) on the thermal properties and crystallization behavior of PHBV/$PR(CO_2)$ blends will be discussed in detail. Chemical structures of PHBV and $PR(CO_2)$ are shown in Figure 1.

2. Experimental

2.1 Materials

Poly(hydroxybutyrate-co-hydroxyvalerate)(PHBV) (15 mol% HV content) used in this study was obtained from Hongzhou Tian'an Bioproducts Ltd. Co., P.R.C.. The characteristics of PHBV are shown in Table 1.

Table 1. Characteristics of PHBV sample.

Sample	HV Content(%)	$\overline{Mw}$ [1]	$\overline{Mn}$ [1]
PHBV	15	4680000	268000

[1]Supplied by the source factory.

$PR(CO_2)$ used in this study was supplied by Changchun Institute of Applied Chemistry Chinese Academy of Sciences.

2.2 Preparation of Samples

PHBV was dried in vacuum at 80° C for 24 h. Then PHBV and $PR(CO_2)$ were melt blended in DACA microcompounder at 175° C for 15 min, which is a discontinuous twin-screw compounder in a 4.5ccm scale. The screw speed was 75rpm. The composition and the code of the blends investigated are given in Table 2.

Table 2. Composition and code of PHBV/$PR(CO_2)$ blends.

Code	PHBV	P90	P80	P70	P60	P40	P30	P20	P10	$PR(CO_2)$
Blend composition PHBV/$PR(CO_2)$ (wt % ratio)	100/0	90/10	80/20	70/30	60/40	40/60	30/70	20/80	10/90	0/100

2.3 Polarized Light Microscopy (PLM)

The growth of PHBV spherulites in the blends were observed with an Olympus BX51 polarized light microscope, equipped with a hot stage and an Olympus exposure control unit. Sample sandwiched between two thin glass slides were melted for 1 min on a hot-plate preheated at 190°C. It was then quickly transferred onto the hot stage of the microscopy, which was maintained at a desired temperature (T_c). The sample was allowed to crystallize isothermally.

2.4 Differential Scanning Calorimetry (DSC)

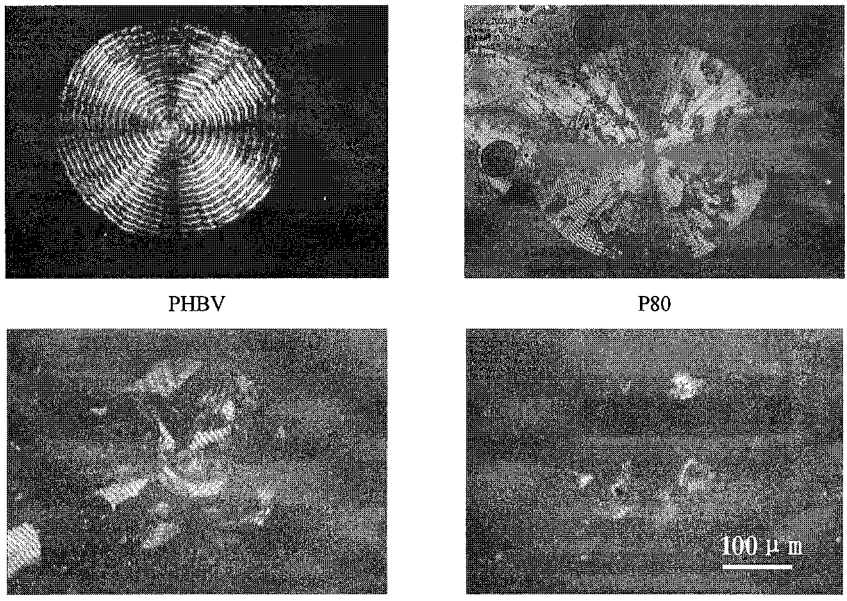
The thermal properties of all samples were analyzed by using a Mettler differential scanning calorimeter, Toledo Star System. Temperature calibration was performed using indium [melting temperature (Tm)=156.6°C, ΔHf=28.5J/g]. To measure the melting temperature and crystallization temperature of PHBV/RE blends, blend samples of 5 to 10 mg were heated in a nitrogen atmosphere from -50°C to 200°C at heating rate of 10°C/min and then cooled to 0°C at a rate of 10K/min.

3. Results and Discussion

3.1 Crystallization Behavior of PHBV/PR(CO_2) Blends

Figure 2 shows a series of optical micrographs of the PHBV/PR(CO_2) blend system. In Figure 2, PHBV shows the typical black cross under PLM. In PHBV/PR(CO_2) blends there are several black areas within the spherulites, which could be caused by PR(CO_2) penetrating to the spherulites of PHBV or light barriers by PR(CO_2) and PHBV distributed in different layers. The influence of impurity on the growth of spherulites of the pure PHBV is shown in Figure 3. In Figure 3(a), it can be seen that the spherulite of PHBV does not grow in a beeline when it comes into contact with impurities. As shown by Figure 3(a), spherulite of PHBV grows along the edge of impurity. The complete spherulite of PHBV contained impurity is shown in Figure 3(b). In Figure 3(b), no concentric ring like patterns

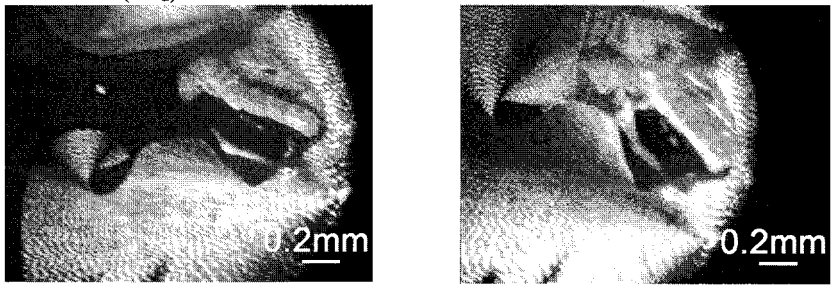
appeared. In contrast to this, the concentric ring like patterns appeared on the spherulites of P80, P40 as shown in Figure 1.. So the black areas on the appearance of spherulites in PHBV/PR(CO_2) blends should be caused by light barriers by PR(CO_2) and PHBV distributed in different layers, i.e., PR(CO_2) did not enter the spherulite in PHBV/PR(CO_2) blends.



PHBV P80

P40 P20

Fig. 2. A series of optical micrographs showing the spherulitic morphology of PHBV/PR(CO_2) blends with PR(CO_2) content.



(a) (b)

Fig. 3. The influence of impurity on the growth of spherulite of the pure PHBV.

The spherulite diameter of PHBV in the PHBV/PR(CO_2) blends was measured. It can be seen the change of the spherulite diameter of PHBV with time is linear (illustrated as Fig. 4). Thus the spherulite growth rate of PHBV can be calculated from the slope. Table 3 shows the spherulite growth rates of PHBV in the PHBV/PR(CO_2) blends. The spherulite growth rate of PHBV in the blends is higher than that of the pure PHBV. And the spherulite growth rates (SGR) of all blends are faster than that of pure PHBV, and decreases slightly with increasing PR(CO_2) weight fraction.

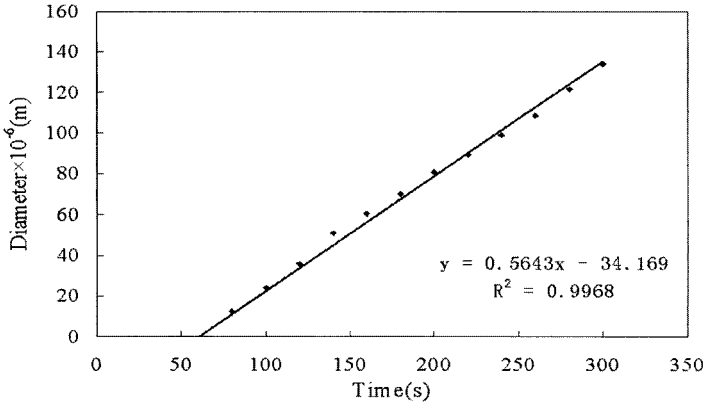


Fig.4. PHBV spherulite growth linear fit.

Table 3. The spherulite growth rate (SGR) of different samples.

Samples	PHBV	P90	P80	P70	P60	P40
SGR (m/s)	5.6×10^{-7}	9.7×10^{-7}	9.6×10^{-7}	8.6×10^{-7}	8.1×10^{-7}	8.0×10^{-7}

3.2 Thermal Behavior of PHBV/PR(CO_2) Blends

Thermal behavior of PHBV/PR(CO_2) blends was studied using DSC. Figure 5 shows the DSC heating thermograms of different PHBV/PR(CO_2) blends. In Figure 5(a), it can be seen that the T_g of the PR(CO_2) is almost unchanged at about 45° C in the blends. This result indicates that the blends of PHBV and PR(CO_2) are immiscible under the mixing

condition. Y. S. Chun and W. N. Kim have studied the thermal properties of PHBV/poly(ε-caprolactone) (PCL) blends[12]. They have reported that the ΔC_Ps of PHBV in the PHBV/PCL blends was too small to be detected clearly since the magnitude of this transition was too low. Therefore, the T_g of PHBV in the PHBV/PR(CO_2) blends which is expected to appear at about 7° C could not be measured by DSC.

In Figure 5(b), there are two melting peaks on both the pure PHBV and the PHBV/PR(CO_2) blends curves. Table 4 summarizes the thermal parameters of PHBV/PR(CO_2) blends as obtained by DSC. The melting temperature of a semicrystalline polymer is primarily a function of the crystal size. So the two melting peaks of the pure PHBV and the PHBV/PR(CO_2) blends resulted from two crystal sizes formed during the quick cooling in the samples preparation. The melting peak at about 150° C resulted from a crystal size that is similar to poly(hydroxyvalerate)(PHV) crystal size. The melting peak at about 170° C resulted from a crystal size that approaches PHB crystal size. The amorphism of PR(CO_2) resulted in no melting peak on the pure PR(CO_2) curve. In addition, it can be seen that the two melting peaks of the P80, P70, P30 and P20 PHBV/PR(CO_2) blends are shifted. That one at 145° C is reduced y about 20K and that one at 170° C is increased by about 10K. These results indicate that the crystal size that resulted in the melting peak at 145° C in the PHBV/PR(CO_2) blends much approaches that of poly(hydroxyvalerate)(PHV). Similarly, the crystal size that resulted in the melting peak at 170° C in the PHBV/PR(CO_2) blends much approaches that of PHB.

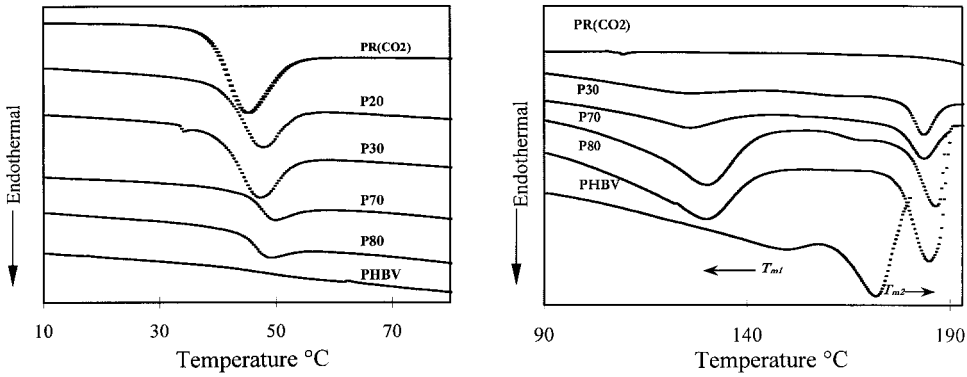


Fig. 5. DSC curves of PHBV/PR(CO_2) blends

Table 4. Thermal parameters of PHBV/PR(CO_2) blends.

Codes	T_{m1}(°C)	T_{m2}(°C)	ΔH_m(J/g)
PHBV	147	172	23
P80	129	184	26
P70	129	186	24
P30	125	183	25
P20	123	183	24
PR(CO_2)	-[1]	-[1]	-[1]

T_{m1}, T_{m2} and ΔH_m are the onsets of lower temperature and higher temperature peaks and the melting enthalpy in Figure 5(b), respectively.

[1] Not detected.

4. Conclusion

As detected by polarized light microscopy and DSC, the blends of PHBV and PR(CO_2) are immiscible under the mixing condition. There are two melting peaks of both the pure PHBV and the PHBV/PR(CO_2) blends and no melting peak of the pure PR(CO_2). The higher temperature melting peak resulted from a crystal size that is similar to PHB crystal size. The lower temperature melting peak resulted from a crystal size that approaches

poly(hydroxyvalerate)(PHV) crystal size. Amorphism of PR(CO_2) resulted in no melting peak of the pure PR(CO_2). In addition, the two melting peaks of the P80, P70, P30 and P20 PHBV/PR(CO_2) blends moved toward the lower and higher temperatures compared with that of the pure PHBV, respectively. It indicates that the crystal size that resulted in the lower temperature melting peak in the PHBV/PR(CO_2) blends much approaches that of poly(hydroxyvalerate)(PHV). Similarly, the crystal size that resulted in the higher temperature melting peak in the PHBV/PR(CO_2) blends much approaches that of PHB. Optical micrographs indicate that PHBV shows typical black cross under PLM, but there are several black areas on the appearance of spherulite in PHBV/PR(CO_2) blends. The black areas on the appearance of spherulite in PHBV/PR(CO_2) blends should be caused by light barriers by PR(CO_2) and PHBV distributed in different layers, i.e., PR(CO_2) did not enter the spherulite in PHBV/PR(CO_2) blends. Furthermore, the spherulite growth rates (SGR) of all blends are similar and higher than that of pure PHBV.

Acknowledgement

This work is financially supported by Shanghai Dawn Project (2000SG27) and Ministry of Education Key Project (No. 00059).

The author wishes to thank "211 Project" of "China Tenth Five Years plan".

[1] F. Gassner, A. J. Owen, *Polymer International*, 1996, 215
[2] E. A. Dawes and P. J. Senior, *Adv. Microbial*, 1973, 10, 138
[3] J. S. Herron, J. D. King and D. C. White, *Appl. Environ. Microbiol.*, 1978, 35, 251
[4] N. G. Carr, *Biochem. Biophys. Acta*, 1966, 120, 308
[5] L. L. Wallen and W. K. Rohwedder, *Enviro. Sci. Technol.*, 1974, 8, 576
[6] A. C. Ward, B. I. Rowley and E. A. Dawes, *J. Gen. Microbiol.*, 1977, 102, 61
[7] D. G. Lundgren, R. Alper, C. Schnaitm and R. H. Marchessault, *J. Bacteriol.*, 1965, 245
[8] P. A. Holmes, L. F. Wright and B. Aldersc, *European patent application,* 1979,15123
[9] J. N. Baptist, *US Patent*, 1962, *3044 942*
[10] Idem, *US Patent*,1962, *3036 959*
[11] R. M. Lafferty, *Chem. Rundsch.,* 1977, *30,* 15
[12] Yong Sung Chun, Woo Nyon Kim, *J. Appl. Polym. Sci.*, 2000, 77(13), 673
[13] Naoyuki Koyama, Yoshiharu Doi, *Macromolecules*, 1996, 29, 5843
[14] Griffin, G. J. L. *Chemistry and Technology of Biodegradable Polymers*, Chapman & Hall: London, 1994
[15] Organ, S. J., Barham P. J., *J. Mater Sci.*, 1991, 28, 1368
[16] Gross R. A., De Mello C., Lenz R. W., Brandl H., Fuller R. C., *Macromolecules*, 1989, 22, 1106
[17] Preusting H., Nijenhuis A., Witholt B., *Macromolecules*, 1990, 23, 4220
[18] Morin F. G., Marchessault R. H., *Macromolecules*, 1992, 25, 576
[19] Avella M., Martuscelli E., *Polymer*, 1988, 29, 1731
[20] Yoon J. S., Choi C. S., Maing S. J., Choi H. J., Lee H. S., Choi S. J., *Eur. Polym. J.*, 1993, 29, 1359
[21] Greco P., Martuscelli E., *Polymer*, 1989, 30, 1475
[22] Azuma Y., Yoshie N., Sakurai M., Inoue Y., Chujo R., *Polymer*, 1992, 33, 4763
[23] Lotti N., Scandola M., *Polymer Bull*, 1992, 29, 407
[24] Gassner F., Owen A. J., *Polymer*, 1994, 35, 2233