

# Effects of Shell Powder on Morphology, Crystallization Behavior and Mechanical Properties in PHBV/Shell Powder Composites

Yang Liu<sup>1</sup>, Yan-mo Chen<sup>1,2</sup>

<sup>1</sup>College of Material Science and Engineering, Donghua University, Shanghai 201620, China;

<sup>2</sup>State Key Lab for Modification of Chemical Fiber and Polymer, Shanghai 201620, China

**Abstract:** Poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) and shell powder are both biodegradable and biocompatible materials. PHBV/shell powder composites were prepared by the melt-blending method. Phase morphology, crystallization, thermal and mechanical properties of PHBV/shell powder composites were investigated by scanning electron microscope (SEM), polarizing optical microscope (POM), differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and tensile test in detail. The results showed that shell powder mostly homogeneously dispersed in the PHBV matrix, and the crystallization behavior of the PHBV/shell powder composites changed with different shell powder content. Moreover, the thermal stability of the composites decreased with the increasing content of shell powder. The tensile strength and elongation at break of the composites were improved compared to neat PHBV.

**Keywords:** PHBV, shell powder, morphology, mechanical property.

## 1. Introduction

Poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) is a kind of thermoplastic material with favorable biodegradable and biocompatible properties, synthesized by microbial fermentation. However, the shortcomings of brittleness and narrow processing window largely limit its applications for environment-friendly plastic [1-6]. As natural biological material, shell powder is good inorganic rigid filler with higher strength and toughness. It plays important roles in modifying desirable performances and reducing the cost [7-9]. In this paper, shell powder was used to reinforce and toughen PHBV matrix by melt blending [10-12]. Our focus was to study the effects of shell powder on the properties of the composites.

## 2. Experimental

### 2.1. Materials

PHBV ( $M_w=4.76\times 10^5$ ,  $M_n=1.12\times 10^5$ ) was provided by Tianan Biomaterial Company with 1.14wt% of HV. Shell powder with particle size of less than  $5\mu\text{m}$  was supplied by Hunan Honghu company.

### 2.2. Specimens preparation

PHBV/shell powder composites with various contents of shell powder were prepared by twin screw extruder and mixers at  $140^\circ\text{C}$ ,  $145^\circ\text{C}$ ,  $165^\circ\text{C}$ ,  $168^\circ\text{C}$ ,  $170^\circ\text{C}$ ,  $170^\circ\text{C}$ ,  $168^\circ\text{C}$ ,  $165^\circ\text{C}$ ,  $165^\circ\text{C}$  and  $160^\circ\text{C}$  from I to X temperature zone respectively and 70 rpm. Before melt blending, all of the materials were completely dried in vacuum oven at  $80^\circ\text{C}$  for 12h. The composites were named by their shell powder content. For example, PHBVS1 indicates the weight ratio of shell powder is

1%, where S refers to shell powder and the number stands for the content of shell powder. After extrusion the composites were injected at  $168^\circ\text{C}$  to obtain specimen samples.

### 2.3 Characterizations

#### 2.3.1 Scanning electron microscope (SEM)

Dispersion of shell powder in PHBV matrix was observed in a JSM-5600LV SEM instrument operating at an accelerating voltage of 5 kV after the specimens were cryogenically fractured in liquid nitrogen and the brittle fracture surface were coated with gold powder.

#### 2.3.2 Polarizing optical microscopy (POM)

An Olympus BX51 polarizing optical microscopy was used to investigate the crystal morphology of the composites. The samples were first heated from  $25^\circ\text{C}$  to  $200^\circ\text{C}$  at  $50^\circ\text{C}/\text{min}$ , and held at  $200^\circ\text{C}$  for 2 min, then cooled to  $70^\circ\text{C}$  at the same speed. The samples were taken photographs every 2 seconds from the beginning of crystallization.

#### 2.3.3 Differential scanning calorimeter (DSC)

Thermal analysis of the composites was characterized by Perkin-Elmer DSC 822e. The samples with the each weigh of 5-10mg were heated in nitrogen atmosphere from  $50^\circ\text{C}$  to  $200^\circ\text{C}$  at a heating rate  $20^\circ\text{C}/\text{min}$  and held at  $200^\circ\text{C}$  for 3 minutes to erase any thermal history, then cooled to  $50^\circ\text{C}$  at a cooling rate of  $20^\circ\text{C}$ .

#### 2.3.4 Thermogravimetric analysis (TGA)

Thermal stability of the composites were performed

by thermogravimetric analysis STA409PC at the speed of 10°C.

### 2.3.5 Tensile tests

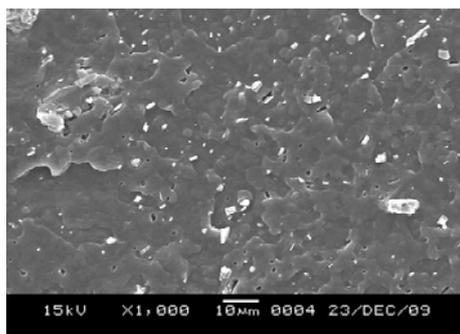
Tensile tests were carried out on a universal testing machine according to ASTM D-638 at room temperature and a crosshead speed of 10 mm/min. The data were the average of four to six samples.

## 3. Results and discussion

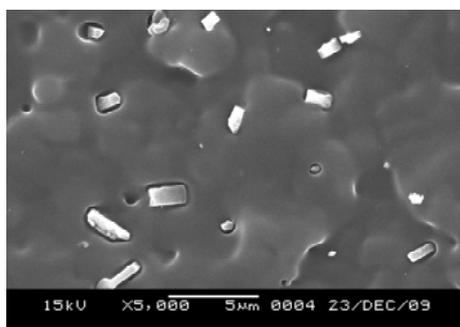
### 3.1 Phase morphology

Fig.1 shows the SEM images of 93/7 (W/W) PHBV/shell powder composite. Obviously, the shell powder mostly homogeneously dispersed in the PHBV matrix; however, a minor conglomeration occurred. It is evident that shell powder particles are lamellar structure and the size is around 2µm.

The crystal morphology of PHBV/shell powder composites was further studied by POM. Fig. 2 displays the spherulitic morphology of the composites with 1% and 3% content of shell powder, respectively. The images were both taken at the sixteenth seconds after the beginning of crystallization. It clearly observes that the number of spherulites in PHBVS3 is more than that of PHBVS1. Moreover, the spherulites of PHBVS3 grow more rapidly. It is indicated that rigid organic particles of shell powder can act as nucleating agent in the composites, which can increase the crystallinity of the composites.

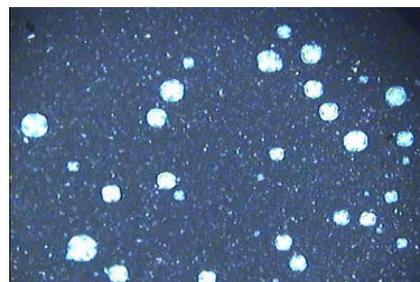


(a)

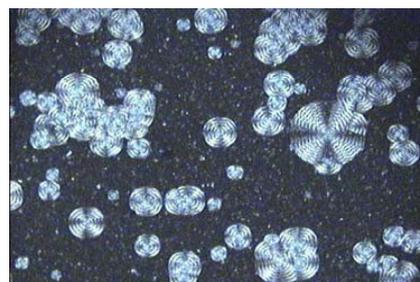


(b)

Fig.1 SEM images of PHBV/S7  
(a) low magnification (b) high magnification



(a)

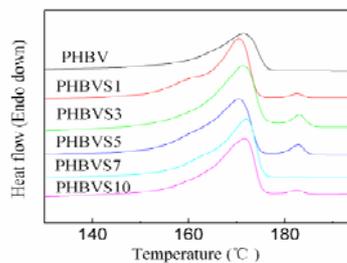


(b)

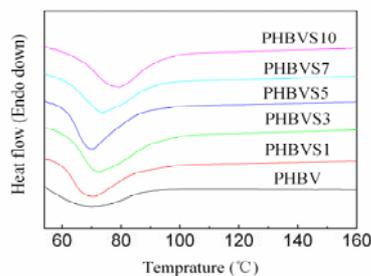
Fig.2 POM images of PHBV/shell powder composites  
(a) PHBVS1 (b) PHBVS3

### 3.2 Crystallization behavior

Fig.3 shows the DSC thermograms of neat PHBV and PHBV/shell powder composites. From the heating curves, it is obtained that the melting points of the PHBV/shell powder composites hardly changed comparing with that of neat PHBV, which was around 171°C. However, the crystallization peak temperature of the composites increased with increase content of shell powder, which was up to 76.89°C when the content is 10%.



(a)



(b)

Fig.3. DSC thermograms of neat PHBV and PHBV/shell powder composites  
(a) heating scans (b) cooling scans

### 3.3 Thermogravimetric analysis

Fig.4 shows the DTG curves of neat PHBV and PHBV/shell powder composites. All the degradation of neat PHBV and the composites with various content of shell powder were single peak curves, which indicates that it is a first order reaction that is typically characteristic of depropagation reaction. It is also found that neat PHBV and all the composites began to degrade at about 233°C and thermal stability decreased with the increasing content of shell powder.

### 3.4 Mechanical properties

The tensile tests were carried out to study the effect of shell powder on mechanical properties in the composites. Table.1 demonstrates the tensile strength, Young's modulus and elongation at break of neat PHBV and the composites in detail. It is found that PHBVS10 has a tensile strength of 31.95MPa, compared to 27.33MPa of neat PHBV, which indicates that shell powder can reinforce the PHBV matrix. Meanwhile the elongation at break of the PHBV/shell powder composites increased with the increasing content of shell powder, highly increased up to 1.62 with respect to 0.98% of neat PHBV.

## 4. Conclusions

In this study, biodegradable composites have been prepared by melt-blending PHBV and shell powder. It is

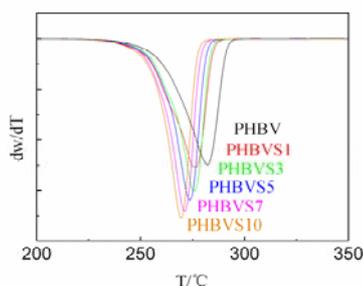


Fig. 4 DTG curves of neat PHBV and PHBV/shell powder composites

Table 1 the mechanical properties of neat PHBV and PHBV/shell powder composites

Sample	Tensile strength (MPa)	Young's modulus(GPa)	Elongation at break (%)
PHBV	27.33	3.21	0.98
PHBVS1	28.54	2.77	1.62
PHBVS3	30.39	3.09	1.51
PHBVS5	31.59	2.97	1.52
PHBVS7	30.11	2.97	1.61
PHBVS10	31.95	3.08	1.58

found that the shell powder mostly homogeneously dispersed and acted as nucleating agent in the PHBV matrix. The melting points of the PHBV/shell powder composites hardly changed compared to of neat PHBV, whereas the crystallization peak temperature of the composites increased with increase of content of shell powder. Thermogravimetric analysis showed the thermal stability of the composites decreased with the increasing content of shell powder. Besides the mechanical properties indicates that shell powder has an effect of toughness and reinforcement on the PHBV/shell powder composites.

## References

- [1] Ma Piming, Wang Shifeng, Wang Ruyin, Zhang Yinxi, Zhang Yong, "Process in Toughening and Plasticization of Poly(hydroxybutyrate) and Poly(hydroxybutyrate-co-hydroxyvalerate)," China Plastics, vol.20, pp.1-7,2006.
- [2] Hobbs J K, McMaster T J, Miles M J, "Cracking in Spherulites of Poly (hydroxybutrate)", Polymer, 37(15):3241-3246,1996.
- [3] McChalicher,C.W.J., Srienc,F., "Investigating the structure-property relationship of bacterial PHA block copolymers", Journal of Biotechnology,vol.132,pp.296-302,2007.
- [4] Wang Weihua, "Process of PHBV biodegradable composites," advanced textile technology,China,vol.4, pp.54-58,2005.
- [5] Wang Wei, Zhang Yu, Chen Yanmo,"Modification of biodegradable material PHBV by blending," Materials Review,China,vol. 20, pp.359-363,2006.
- [6] Ji Lingfang, Yao Jingxia, "Biodegradable materials," Plastics Science & Technology,China, vol.5,pp.52-54,2002.
- [7] Shufang Wang, Cunjiang Song, Guangxin Chen, Tianying Guo, Jing Liu,Banghua Zhang, Shigeya Takeuchi, "Characteristics and biodegradation properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organophilic montmorillonite (PHBV/OMMT) nanocomposite," Polymer Degradation and Stability,China, vol. 87,pp.69-76, 2005.
- [8] Xu Xiaoxu, Zhang Baoyan, Fu Luxiang, "Thermal and mechanical properties of PHBV/CaCO<sub>3</sub> blends," Journal of Northeastern University (Natural Science),China, vol.29,pp. 1061-1064,2008.
- [9] Shuai Wang, Piming Ma, Ruyin Wang, Shifeng Wang, Yong Zhang, Yinxi Zhang, "Mechanical, thermal and degradation properties of poly(d,l-lactide)/ poly(hydroxybutyrate-co-hydroxyvalerate)/poly(ethylene glycol) blend," Polymer Degradation and Stability, China, vol.93, pp.1364-1369, 2008.
- [10] Xu Li, Kerh Li Liu, Miao Wang, Siew Yee Wong, Wuiwui Chauhari Tjiu, Chao Bin He, Suat Hong Goh, Jun Li, "Improving hydrophilicity, mechanical properties and biocompatibility of poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] through blending with poly[(R)-3-hydroxybutyrate]-alt-poly(ethylene oxide)," Acta Biomaterialia, vol.5,pp.2002-2012, 2009.
- [11] Kunyan Wang, Yanmo Chen, Yu Zhang, "Effects of organoclay platelets on morphology and mechanical properties in PTT/EPDM-g-MA/organoclay ternary nanocomposites," Polymer, vol.49, pp.3301-3309, 2008.
- [12] Laiquan Miao, Zhanbin Qiu, Wangtai Yang, Takayuki Ikehara, "Fully biodegradable poly(hydroxybutyrate-co-hydroxyvalerate) /poly(ethylene succinate) blends:Phase behavior, crystallization and mechanical properties," Reactive & Functional Polymers, vol.68, pp.446-457,2008.