MICROCELLULAR FOAMING BEHAVIOR OF BIODEGRADABLE POLY (3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)/POLYLACTIC ACID COMPOSITES

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Abstract
In this paper, Biodegradable poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/polyactic acid (PLA) biocomposites were prepared using the Hakkcr rheometer. We investigated the effect of various PLA content on the PHBV’s thermal properties and on its foaming behavior. The differential scanning calorimetry (DSC) results showed that the presence of PLA facilitate the cold crystallization of PHBV matrix. Along with the addition of PLA, the melt temperature of composites are lower than pure PHBV. SEM results of foamed samples presented that the addition of PLA led to the various foaming morphologies, and cell morphologies was changed from close cell to open cell as increasing the content of PLA in the PHBV matrix. The changed foaming morphology was attributed to the phase morphology and composites melt strength changed, and the resultant mechanism was also proposed.

Introduction
Studies of biobased and biodegradable polymers have attracted increasing attention due to the great demand to reduce dependency on petroleum-based polymers, decrease the accumulation of persistent plastic waste, and better control the emission of CO$_2$ in the environment. In recent years, biodegradable polymers have been demonstrated to be a promising substitute for petrochemical-based polymers, which is due to its good processability, environment-friendly, sustainability and recyclable.

As one of the most widely used biobased polymers, polyactic acid (PLA) can be produced by either ring-opening polymerization of lactide or condensation polymerization of lactic acid monomers produced from renewable resources via a fermentation process. PLA has been used to produce for decades with the hope of replacing the traditional synthetic fibers at least partially because of their good mechanical properties, fully biodegradable, excellent biocompatibility, and good thermal plasticity[1]. However, the market response was far below the expectation due not only to the relatively high price but more critically to the bottleneck in properties. Disadvantages like poor melt properties, brittleness, and low thermal resistance limit its use in different applications. To overcome these problems, several methods were implemented and used to improve the resultant properties in PLA, including blending with other biodegradable polymers [2], plasticization [3], and copolymerization [4]. Among these methods, blending was reported to be the easiest and most cost effective [5]. Polymer blends had been extensively studied because it presents the possibility of enhancing the overall properties of the final material through a synergistic combination of the desirable properties of each component in one system [6-8].

To keep the bio-based and degradable characteristics, we chose one of the commercially available PHAs, poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), to blend with PLA. Since PHBV or its homopolymer poly (3-hydroxybutyrate) (PHB) is close to PLA in chemical structure and processing window, numerous studies have been carried out on the properties and structure of PLA/PHBV or PLA/PHB blends [9-11]. It was interesting that PLA and PHBV or PHB exhibited partial molecular interactions even though they were thermodynamically between PLA and PHBV or PHB would be enhanced with the low molecular weight of the component, low content of PHBV or PHB, or the occurrence of transesterification [12-13]. The physical properties and degradation characteristics of PHBV/PLA blend can be tailored by compounding PLA and PHBV at different biodegradable rates [14-16].

In this study, PHBV/PLA composites were prepared by melt blending, and its microcellular foams were fabricated by a batch foaming process using supercritical CO$_2$ (scCO$_2$) as a physical blow agent. The thermal properties, morphological analysis and foaming behavior of the PHBV/PLA composites were comprehensively investigated. The formation of cell structure in the composite foams was also discussed and proposed.

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**Experimental**

**Materials**

PHBV (grade: ENMAT Y1000P) used in the experiment was purchased from Tianan Biological Material Company, Ltd. (China, Ningbo), which has Mw = 387000 g/mol, and an ENMAT Y1000P content of 3% hydroxyvalerate. PLA (4032D) containing 1.2-1.6% D-LA were purchased from Natureworks, USA. It has a weight-average molecular weight (Mw) of 207 kDa and a polydispersity index of 1.74. Industrial-grade CO₂ was used with purity of 99.5% and received from Shengtong Company in China. The chemical structures of the two polymers used for the blends are illustrated in Scheme 1.

**Scheme 1. Illustration of the Chemical Structure of the Two Polymers**

\[
\begin{align*}
\text{PLA} & : \text{CH}_2 \text{CH} \text{O} \text{CH}_2 \text{CH}_2 \text{O} \text{CH}_2 \text{CH}_2 \text{O} \\
\text{PHBV} & : \text{CH}_3 \text{O} \text{CH} \text{CH} \text{C} \text{H}_3 \text{O} \text{CH} \text{CH} \text{C} \text{H}_3 \text{O}
\end{align*}
\]

**Preparation of the PHBV/PLA composites**

The PHBV and PLA were dried under the vacuum at 80 °C for 4 h prior to use. And then, PHBV/PLA blends at various ratios (70/30, 50/50, 30/70 w/w) were compounded by using HAKKE rheometer. The process temperature sets as 190 °C for 5 min and the speed 50 rpm. In order to have a better comprehension, the whole samples obtained with the content of PLA (30%, 50%, 70%) were named as 70/30, 50/50, 30/70.

**Preparation of the foaming samples**

Due to the foaming process requirements, the strings were processed into compress-molded plates using a hot press (CH-0203, China), preheating at 190 °C for 8 min, followed by heating compressing for 6 min at the same temperature and subsequent cooling under pressure for 6 min.

The foaming behavior of PHBV/PLA was investigated by a home-made foaming device with Supercritical CO₂. The Carbon dioxide was used as the physical blowing agent. From the past studies about pure PLA foaming, samples were saturated under the melting point (such as 150 °C). The samples were soaked for 2 hours and then cooled to 100 °C and 110 °C individual to fast depressurize. After the pressure relief, the foam specimen was solidified by the water-cooling system for short time.

**Measurements**

The differential scanning calorimetry (DSC) was performed on a Netzsch 204C (Germany) equipped with liquid nitrogen cooling system. The melting temperature (T_m), cooling crystallization temperature (T_c), crystallization temperature (T_g) and glass transition temperature (T_g) of the composites as well as their enthalpy of crystal fusion (ΔH_c and ΔH_m) was obtained from the curves. The samples of 5-10 mg were dried in a vacuum oven before they were sealed in aluminum crucibles. At first, the samples were heated from room temperature (25 °C) to 200 °C and kept isothermal for 5 min to exclude any thermal history, and then cooled down from 200 to 25 °C at a cooling rate of 10 K/min and maintained for 5 min. Subsequently, they were heated again to 200 °C at 10 K/min.

Morphologies of the PHBV/PLA composites were studied using scanning electron microscopy (SEM). The compression-molded samples and foamed samples were also immersed in liquid nitrogen for 1 hour and then fractured in it. After that, all the brittle fractured surfaces were sputtered with a gold payer.

**Results and discussion**

**Differential Scanning Calorimetry**

The physical, mechanical, and thermal resistance properties of these polymers are extremely dependent on the solid-state morphology and its crystallinity. Accordingly, it is very important to study the influence of the existence of the other component on the crystallization of matrix polymers in the blend. Fig. 1(a) shows the second heating scans and Fig. 1(b) shows the representative thermograms obtained from the first cooling scans, and the results are summarized in Table 1. The glass-transition temperature (T_g) data were taken as the end temperatures of the glass transition region. The T_g of pure PLA was about 64.3 °C, whereas the T_g values of the PHBV/PLA composites were lower than that of the pure PLA. This was because the addition of PHBV increased the mobility of the PLA chains.

Compared with the neat PLA, the enthalpy of cold crystallization (ΔH_c) at the heating process of PLA in the blends was found to increase. These results indicate that the cold crystallization of PLA is promoted by the addition of PHBV. In general, cold crystallization took place at a temperature above the T_g of the blends at which the crystallizable polymer chains possessed enough

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segmental mobility to crystallize. The enhancement of cold crystallization of PLA by the addition of PHBV can be attributed to the following reason. First, the amorphous phases of PHBV could activate the chain mobility of PLA. If there is sufficient chain mobility locally activated, the cold crystallization will be improved due to the easily dynamic chain alignment. Second, the surface of the PHBV phase might also act as a nucleating center so that enhance the crystallization of the PLA in the blends [17-18]. PHBV/PLA binary blend is a system with some degree of compatibility. Therefore, it is reasonable to speculate that the presence of PHBV phase could play a role of nucleation of PLA. As shown in Table 1, pure PHBV showed an obvious Tm at about 172.9, and Tm of PHBV/PLA blends reduced with the increase of PLA content.

Table 1. Thermal properties of PHBV, PLA and PHBV/PLA composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg (°C)</th>
<th>Tcc (°C)</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
<th>ΔHc (J/g)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHBV</td>
<td>—</td>
<td>117.6</td>
<td>172.9</td>
<td>—</td>
<td>78.98</td>
<td></td>
</tr>
<tr>
<td>70/30</td>
<td>62.5</td>
<td>98.3</td>
<td>116.3</td>
<td>172.8</td>
<td>4.382</td>
<td>61.54</td>
</tr>
<tr>
<td>50/50</td>
<td>62.2</td>
<td>110.1</td>
<td>117.7</td>
<td>170.8</td>
<td>5.908</td>
<td>48.64</td>
</tr>
<tr>
<td>30/70</td>
<td>62.2</td>
<td>107.7</td>
<td>119</td>
<td>170.2</td>
<td>18.42</td>
<td>26.62</td>
</tr>
<tr>
<td>PLA</td>
<td>64.3</td>
<td>—</td>
<td>—</td>
<td>167.1</td>
<td>—</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Foaming Behavior

As is well-known, the types of morphology and the size of dispersed phases in the polymer blends are important factors that determine physical properties and rheological behavior. Furthermore, phase morphology can provide the relationship between microstructure and the mechanical properties. Therefore, the detailed phase morphology of the blends was studied by SEM method. Figure 2 presents the SEM micrographs of cryo-fractured surfaces of PHBV/PLA binary blends. The immiscible morphology of the PHBV/PLA (70/30) blend became miscible when the content of the PLA increased to 50%. The diameters of the dispersed minor phases of 70/30 with PHBV as matrix were bigger than that of 30/70 with PLA as the matrix. A typical co-continuous phase morphology with PHBV and PLA was observed for blends PHBV/PLA 50/50. When the content of PLA changed, disperse phase morphology was observed again.

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increases and restricts the cell growth, resulting in small cell size and thick cell walls. On the contrary, if the temperature is too high, the low melt strength will cause cell wall rupture and collapse and lead to low expansion ratio. In this study, two foaming temperatures (100, and 110°C) were used to investigate the foaming behavior of PHBV/PLA blends.

Figure 3 shows the structures of PHBV/PLA blends after foaming. It can be seen that 70/30 foams exhibited varied cell structure with almost closed cell walls. This phenomenon is typical because the cell only occurs on PLA phase but not PHBV phase. Therefore, the cell size depends on the diameters of the PLA dispersed phases. The 50/50 foams showed the sandwich-like cell structure. With the increase of PLA content, separated structure was changed to co-continuous structure and large cell density tended to be obtained. As it showed in Figure 2(b), PHBV and PLA dispersed layer by layer, so that it causes the particular cell structure. Generally, foaming at low melt strength, it will be easier to achieve thin cell wall and more open cells. In our early study, PHBV melt strength is higher than PLA. Therefore, it was found that 30/70 foams were the optimal PLA ratio to achieve the highest cell opening rate. According to the results discussed above, a schematic representation shown in Figure 4 is proposed to help understand the effect of PLA content on composites foaming.

![Figure 3. SEM micrographs of PHBV/PLA blend foams under two foaming temperatures. 70/30: (a) 100 °C, (a’) 110 °C. 50/50: (b) 100 °C, (b’) 110 °C. 30/70: (c) 100 °C, (c’) 110 °C.](image)

**Conclusions**

In this study, biodegradable poly (3-hydroxybutyrate-co-3-hydroxy-α-valerate)/polylactic acid composites have been prepared via Hakker Rheometer. According to the DSC curves, we found that the PLA glass transition temperature reduces to 62.2 °C due to the addition of PHBV. The effect of incorporation of the PHBV, the enthalpy of cold crystallization of PLA increase to 18.42 J/g. From the SEM results, the immiscible morphology of the PHBV/PLA (70/30) blend became miscible when the content of the PLA increased to 50%. The foaming samples show that with the different content of PLA, cell morphology was changed. 70/30 foams exhibited varied cell structure with almost closed cell walls typically. Meanwhile, 50/50 foams showed the sandwich-like cell structure and 30/70 presented open cell structure. We concluded that the more PLA, the more composites compatibility have. Certainly, we can control the cell structure by changing the content of PLA so that foaming sample will has more extensive application in the future.

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