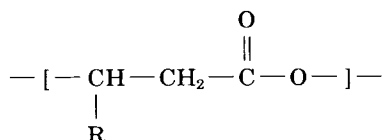


# NOTE

## Polyhydroxybutyrate Produced from Cheap Resources. I. Crystallization and Melting Behavior

### INTRODUCTION

Polyhydroxybutyrate is an important member of a polymer family named polyhydroxyalkanoates whose molecular formula is given as follows:



R: CH<sub>3</sub> polyhydroxybutyrate (PHB); R: CH<sub>2</sub>CH<sub>3</sub> polyhydroxyvalerate (PHV). In recent years, PHB has attracted global attention because of its unique properties when used as a thermoplastic. These properties include biodegradability<sup>1,2</sup> and producibility from renewable resources. It is now commercially available through a number of chemical companies such as ICI, Sigma, etc., and has been tried in many potential application areas such as disposable personal hygiene, packaging, and biomedical materials.<sup>3</sup>

The prevailing method of producing PHB is bacterial fermentation. Various species of bacteria can accumulate PHB when fed with certain carbon sources like glucose.<sup>4</sup> However, the market price of PHB has been rather high. This is primarily due to production costs much higher than those of olefin plastics, thus preventing using PHB in large-scale applications, especially the practical possibility of using it as a biodegradable agrarian membrane. One way to solve this problem is to reduce raw material costs, i.e., employing cheaper and more abundant carbon sources like methanol and some agricultural byproducts such as maize pulp, molasses, and sugar beets, which are particularly noteworthy to those countries lacking sufficient oil reserves.<sup>5</sup> In this article, we examined some crystalline and melting properties of PHB and PHB-PHV (3%, DSC analysis only) produced from methanol and acid hydrolysate of maize pulps and compared them with those of PHB commercial products and literature data.

### EXPERIMENTAL

#### Materials

Polyhydroxybutyrate (PHB), with a 100% purity and molecular weight of  $1.94 \times 10^5$ , was bacterially produced using methanol and maize pulp acid hydrolysate by the Chengdu Institute of Biology, Chinese Academy of Sciences. A tiny amount of a PHB-PHV (3%) copolymer was similarly produced by the Beijing Agriculture University. Both samples were white fibrous powder and were tested as received. A small amount of PHB purchased from Sigma was used in the DSC analysis for comparison.

#### Methods

**Differential Scanning Calorimetry Analysis.** PHB homopolymer, PHB-PHV (3%) copolymer, and PHB from Sigma were tested on a CDR-1 DSC analyzer (Shanghai Balance Instrument Co.). The analyzer was preheated and calibrated by a calorimetric standard substance. The fibrous samples, about 10 mg each, were loaded into aluminum pans and DSC curves were recorded with a heating rate of 5°C/min, calorimetric amplification range of  $\pm 100 \mu\text{V}$ , and upper heating temperature of 200°C. Melting points and fusion enthalpies were calculated from the curves. At the same time, a melting point detector equipped with a polarized light microscope was used in order to provide some comparative data.

**Qualitative Measurements of Melt Index.** PHB homopolymer was tested on a XRZ400-1 melt indexer (Jilin University Mechanical Plant). After being preheated, about 1.5 g of the sample was quickly loaded into the heating barrel (inner diameter  $9.554 \pm 0.004$  mm), then gradually heated to  $182.0 \pm 0.2^\circ\text{C}$  within 15 min and maintained there for 10 min. During the course of heating, the sample was constantly compressed to remove air remaining in fiber spaces. When the height of the sample reached 1.78 cm, the density was approximately 1.16, which was considered to be the most suitable for obtaining usable results. About 5 kg weight was added. The extruded sample was cut into segments every 1 min and accurately

weighed after being cooled to room temperature. Finally, the barrel temperature was calibrated by standard thermometers (VEB MLW Prüferäte-Werk Medingen, Sitz Freital, the former East Germany).

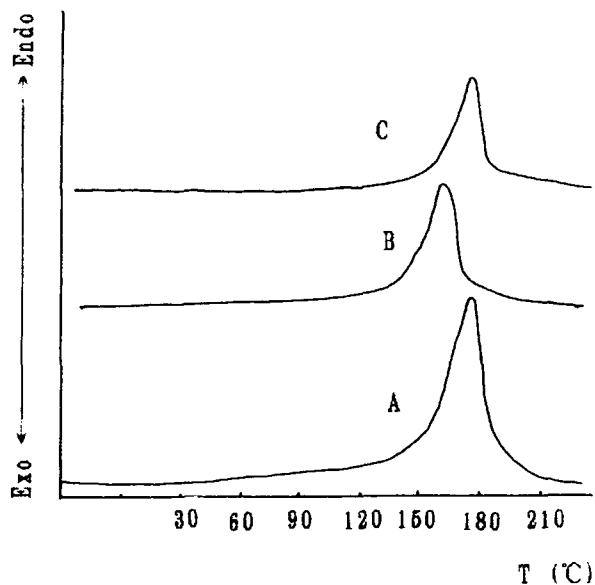
**Optical Polarimetric Analysis.** A JJY-1 crystallization rate detector (Institute of Chemistry, Chinese Academy of Sciences) was used to record the variation of the transmitted polarized light intensity of PHB samples vs. the time under certain crystallizing temperatures.

A certain amount of PHB was put on a thin glass layer and was melt at 210°C for 10 min. At the same time, it was covered by another glass layer to form a circular membrane with an approximate diameter of 10 mm and thickness of 0.1 mm. After cooled to room temperature, it was fastened on sample clips and heated to 210°C and maintained there for 40 s. After that, the sample was immediately immersed into a crystallization bath and the variation curve of light intensity vs. time was recorded. When the fluctuation of the light intensity was negligibly small, the sample piece was removed by another piece for testing at another crystallizing temperature.

## RESULTS AND DISCUSSION

### DSC Analysis

Figure 1 shows the DSC curves of PHB (100%), PHB-PHV (3%), and PHB (Sigma). In all cases, the fact that only one endothermic peak is dominant suggests that all samples produced are highly crystallized. Some extent of broadening of the melting peaks can be seen from the three curves. There could be two explanations for this:



**Figure 1** DSC curves of PHB samples with a heating rate of 5°C/min: (A) PHB (100%); (B) PHB-PHV (3%); (C) PHB (Sigma).

**Table I** Melting Points (Measured by Two Different Methods) and Enthalpies of Fusion of PHB Samples

Samples	Mp (°C)		$\Delta H_m$ (cal/g)
	DSC	Mp Detector	
PHB (100%)	177–179	177.3	28.2
PHB-PHV (3%)	164–165	169.0	24.1
PHB (Sigma)	178–179	178.9	22.6

One is that the polymers were degraded while being melt; the other is that the broadening is due to the reorganization behavior of some noncrystallized areas existing in highly crystallized samples. But since 5°C/min is not regarded as a high enough heating rate under which the thermal effect of reorganization of the less stable chains might interfere with the main melting peak, the first reason should be more plausible, i.e., the thermal degradation occurred almost simultaneously with the melting process. Its thermal effect is confused with the dominant fusing peak and is impossible to be distinguished. There are probably two reasons for the degradation: One is thermoxy decomposition between the fibrous sample surface and air; the other is that a tiny amount of moisture contained in the fibrous sample caused the polymer chain to break up. The moisture is absorbed unavoidably during experimental manipulations like sample loading.

The melting point ranges and enthalpies of the three samples are given in Table I. The former is compared with the not-so-exact values obtained from the polarized light microscope observations and the literature.<sup>6</sup> It can be seen that the data of the PHB (100%) are remarkably close to those of the Sigma product. There is a 13–14°C decrease in the melting points from the PHB homopolymer to the PHB-PHV (3%) copolymer, thus confirming the view that the addition of hydroxyvalerate units into the PHB molecular structure can result a lower melting point,<sup>3</sup> so that the processing may become easier.

### Melt Index Measurements

Practically, the melt index is regarded as a relative value of viscosity of a melted compound and is often being referred to when the fluidness of a certain polymer needs to be evaluated in the plastic processing industry. Being a qualitative parameter, the melt index is significant only when being empirically associated with processing conditions and properties of the end product. However, except for the lower shear rate under which the measurement was made, the melt index measuring procedure is much like the manipulations carried out in actual melt spinning and melt extrusion. It does not require sophisticated instrumentation and does not demand large quantities of the sample. Therefore, it is still quite valuable in providing

some perceptual understanding about PHB's behavior in further processings.

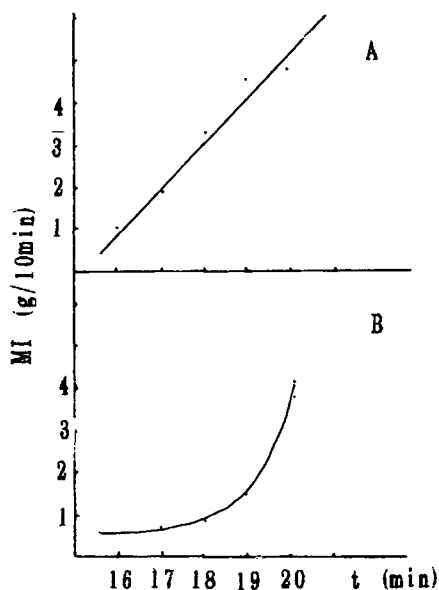
Figure 2 shows the trend of melt index changes with time at the temperatures of  $182.0 \pm 0.2^\circ\text{C}$  and  $184.0 \pm 0.2^\circ\text{C}$ . It is known that for a thermoplastic polymer with a stable molecular structure the melt index should be a constant under proper detecting conditions, which include a temperature higher than the flowing point and lower than the degradation point. But it is not the case in PHB, as we have discovered that at a set temperature the melt index ascends with time. This indicates that the fluidity or melt viscosity diminishes with heating time. The obvious explanation for this is the occurrence of thermo-degradation due to the contact with oxygen and absorbance of moisture and this coincides with the results of DSC analysis. It is also noted that the tendency of melt index variation at  $182.0 \pm 0.2^\circ\text{C}$  is primarily linear, whereas at  $184.0 \pm 0.2^\circ\text{C}$ , it soars up like an index. This indicates that the sample fluidity changed considerably even after a  $2^\circ\text{C}$  fluctuation in temperature. It is thus concluded that the melting property of PHB is markedly sensitive in the vicinity of the melting point.

### Optical Polarimetric Analysis

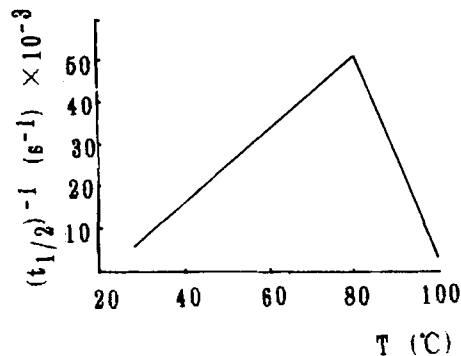
The curves of polarized light intensity of PHB vs. time are recorded. From the Avrami equation that depicts the crystallization of polymers, we have

$$1 - C = e^{-kt^n}$$

where  $C$  is the crystallinity;  $k$ , a constant;  $n$ , the Avrami constant; and  $t$ , the time. When the contribution of spher-



**Figure 2** Melt index variations with heating time at (A)  $182.0 \pm 0.2^\circ\text{C}$  and (B)  $184.0 \pm 0.2^\circ\text{C}$ .



**Figure 3** Crystallization rate of PHB (100%) sample vs. temperature curves. The largest rate is at  $80^\circ\text{C}$ .

ulite birefractance is solely considered, the nucleation and crystalline growth rate are in direct proportion to the polarized light intensity, i.e.,

$$(I_\infty - I_t)/(I_\infty - I_0) = e^{-kt^n}$$

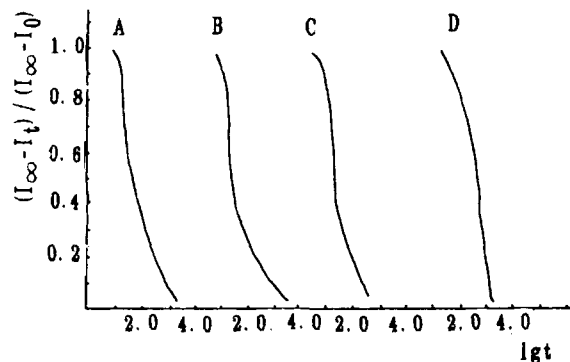
where  $I_t$ ,  $I_0$ , and  $I_\infty$  are light intensities of time  $t$ , zero, and infinity, respectively.

Figure 3 shows the relationship of the crystallization rate and temperature. For convenience, the parameter  $(t_{1/2})^{-1}$  is used to characterize the crystallization rate of the polymer, where  $t_{1/2}$  is the time when light intensity equals  $(I_\infty + I_0)/2$ . It is obvious that the largest rate appears at  $80^\circ\text{C}$ , which is in accordance with the literature.<sup>7</sup>

Figure 4 shows the relationship of crystallinity and time at different temperatures. This group of curves with inverse "S" shapes can be overlapped if paralleled along the  $lgt$  axis.

### CONCLUSIONS

The primary thermal properties and crystalline behaviors of PHB bacterially produced from cheap resources like methanol and maize pulp acid hydrolysate are similar to



**Figure 4** Crystallinity vs. time curves of PHB (100%) sample at different temperatures: (A)  $40^\circ\text{C}$ ; (B)  $60^\circ\text{C}$ ; (C)  $80^\circ\text{C}$ ; (D)  $100^\circ\text{C}$ .

those of commercial PHB products manufactured from costly carbon sources. The data of melting points, fusion enthalpy, and temperature of largest crystallization rate support this result. Additionally, when heated, all the PHB samples showed remarkable unstability and degradation enhanced by oxygen and moisture. The flowing property of the melt polymer is also found to be sensitive to temperature variation. Therefore, effective means must be employed to isolate the sample bulk from oxygen and undertaken to seek proper processing conditions in order to expedite the wide application of this low-cost biodegradable plastic.

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