

INFLUENCE OF HV UNITS OF PHB-HV COPOLYMER SYNTHESIZED BY *Ralstonia eutropha* ON THE THERMAL PROPERTIES

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Introduction

Since many years ago, poly(hydroxyalkanoates) (PHAs) have attracted attention in industrial researchers as a possible candidate for large-scale production due to its interesting properties. It has been reported that certain properties of the poly (3-hydroxybutyric-3-hydroxyvaleric acid) (PHBHV) copolymer are dependent on mole fractions of the monomers units, HB and HV, in PHBHV [1]. In this paper, we showed the effect of fed composition (butyric acid and valeric acid) on the HV content in the PHBHV, moreover correlated this composition with the thermal properties of bacterial (PHBHV).

Materials

The polymers PHB and PHBHV were produced in fed-batch cultures with *R. eutropha* ATCC 17699 from methods previously published [2]. The feeding rate used in the fermentations was based on the previous work of Shimizu et al [3] to control of the HV units and allow the level of organic acid below of the inhibition concentration. Different proportions of organic acids were submitted to obtain copolymers with different proportion of HV units. The rates fed of fresh medium in the fed-batch phase were in all cases 50 mL/h. The copolymers obtained and used in the experiments presented a range of HV of 0 to 47 % mol.

Purification of polymers

PHB and PHBHV samples were purified as followed: the cells were harvested by centrifugation and then freeze-dry. After the materials were extracted from the dried cells with hot chloroform in a Soxhlet and precipitated with hexane, redissolved in chloroform and precipitated with hexane and then dried in a vacuum oven to remove the residual solvent.

Characterization of polymers

The percentage of HV units in the samples was determined by ¹H NMR (300 MHz, Varian Mercury) and compared with results obtained by gas chromatography (CG Tracor, FID, AT-1000column, injector temperature 160°C) (see Table I).

TGA and DSC experiments

Thermal stability of the samples was carried out in a Thermobalance and DSC Perkin-Elmer 7 model using 1 ±0.2 mg at a heating rate of 10 °C min⁻¹ under flux of nitrogen (30 mL min⁻¹).

Results and Discussion

Thermogravimetric experiments were carried out on three samples (PHB and two copolymers) and the samples are stable up to 200 °C as show n Figure 1. The homopolymer sample is the most thermally stable. The dependence of Tg and crystallinity (χ with % HV is shown in Table I. Tg values decrease as % HV units in the copolymer increase, but this decrement is low (0.6 °C for 0 % to -7.4 °C for 38 %).

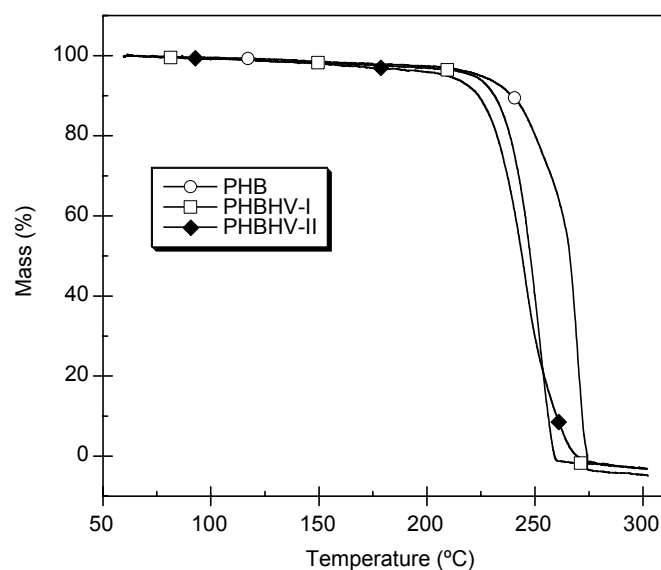


Figure 1. Thermal stability for the three samples: PHB and two PHBHV copolymers.

Table I. DSC and X-Rays results for the samples tested.

Sample	HV (%)	T _g (°C)	T _{f1} (°C)	T _{f2} (°C)	χ (%)
PHB (A)	0	-2.0	179	-	76
PHBHV (B)	7	-2.0	130	n. o.	62
PHBHV (C)	21	-4.0	85	n. o.	52
PHBHV(D)	24	0.6	98.4	167.7	75
PHBHV (E)	35	-6.6	74.8	170.2	60
PHBHV(F)	38	-7.4	74.0	169.0	61
PHBHV(G)	48	-8.0	T. U.	T. U.	52

T. U. Thermally unstable. n. o. = not observed

Figure 2 shows three thermograms of the PHB sample, after 14 hours of quenching. The first thermogram only showed a fusion peak. In the second and third heating, this peak shifts to a lower temperature and height. The second heating also shows a crystallization peak, which increases in the third heating. The results showed, clearly implies a high degree of incorporation of comonomers within the lattice, this is true if it considerate that the amorphous phase changes independently of crystallization temperature.

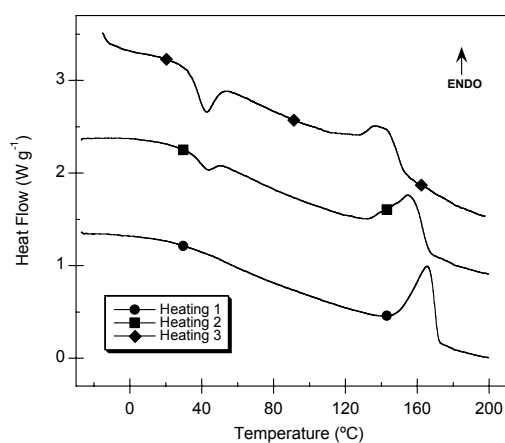


Figure 2. DSC thermograms of the PHB sample (The firsts three heating).

Figure 3A shows a microphotograph of the PHB sample at the end of the crystallization process during the fourth heating (not shown in Figure 3). The spherulites are well defined, although not completely formed. Figure 3B shows the morphology of the PHB sample, which was quenched for 4 hours at 80°C, cooled to ambient temperature, heated to crystallization, and finally cooled at 10 °C/min. In this case, the spherulites were well defined.

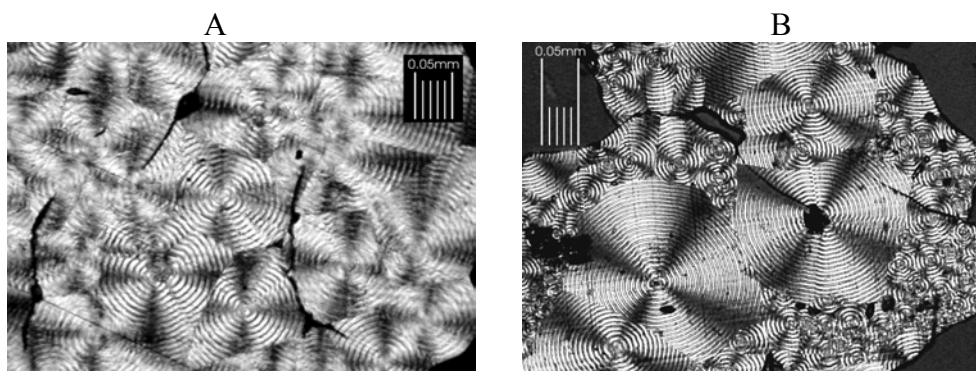


Figure 3. Microphotograph of the PHB sample: (A); after of end the crystallization process during the heating, (B); After the crystallization when cooling the sample (quenching for 4 h at 80 °C).

According to Barker et al [4], this kind of copolymer shows co-crystallization because the spherulites crystallize into a PHB structure [5].

Conclusions.

The percentage of HV units in the copolymers shows a linear effect on the glass transition. The regimen of feeding do not have an effect on the comonomer distribution, always is random. The crystalline lattice of these copolymers is independent of the crystallization temperature, whereas the compositions in the crystalline phase changes

References

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